# Deuterium NMR Studies of Water in Oriented Nylon 6 Fibers

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*Received October 3, 1995; Revised Manuscript Received May 14, 1996*[⊗]

ABSTRACT: Deuterium NMR studies of drawn nylon 6 fibers hydrated with $D_2O$ suggest the presence of three types of water and two classes of exchangeable protons. The water exhibits varying degrees of residual orientational order (incompletely averaged quadrupolar interactions) as well as drying characteristics that enable a comparison with interlamellar and interfibrillar water previously defined by small-angle neutron scattering.[1] The interfibrillar water is bound the strongest and exhibits the largest (draw-ratio-dependent) quadrupolar splitting in aligned fibers. Dry fibers (whose accessible amide protons have been deuterium exchanged with $D_2O$) show anisotropic powder spectra. The angular dependence of these spectra suggests that two distinct classes of amide deuterons contribute to the spectra, one associated with aligned interfibrillar amorphous chains (with N−D bonds on average normal to the fiber axis) and more isotropic deuterons probably associated with chain folds and variously oriented crystallite surfaces.

## Introduction

Recently, small-angle neutron scattering (SANS) was utilized to delineate the morphology of hydrated, semicrystalline nylon 6 fibers by using $D_2O$ as the contrasting agent.[1,2] Water diffuses almost exclusively into the amorphous phase,[3,4] and by exploiting the scattering length differences between hydrogen and deuterium, the distribution of water within the fiber gave a coarse image of its morphology. We anticipated that nuclear magnetic resonance (NMR) might complement the SANS image as the motional characteristics of the water in the oriented amorphous phase should be a sensitive function of the disposition of interfacial chains—chemical exchange and restricted diffusion will lead to anisotropic motion and incompletely averaged NMR interactions. If $D_2O$ is used as an indirect probe of the fiber morphology, its deuterium NMR ($^2$H NMR) spectral features will be dominated by the averaged quadrupolar interaction. In uniaxial systems this averaged interaction enables one to measure the degree of residual orientational order of the water resulting from anisotropic reorientational diffusion and proton (deuteron) exchange within the partially aligned amorphous phase in drawn fibers. This technique was employed before in hydrated collagen fibers,[5,6] rayon fibers,[7] and oriented polyethylene.[8] Herein we study the behavior of $D_2O$ in hydrated nylon 6 as a function of fiber draw ratio with $^2$H NMR. We find evidence for three types of water—isotropic water and two classes of water with different amounts of draw-ratio-dependent residual order. Additionally, the accessible N−H groups in the amorphous phase and on crystal surfaces undergo deuteron exchange. Hence, broad-line $^2$H NMR of partially exchanged and subsequently dried fibers gives more direct microscopic information about the influence of drawing on fiber morphology.

In nylon 6 fibers there are two resonably distinct categories of amorphous domains: interlamellar (the ∼30 Å gap between the folded chain interfaces of a stacked pair of crystalline lamellae) and interfibrillar (extended chains and longitudinal voids surrounding ∼50 Å diameter fibrils).[1,9] Both regions are intrinsically anisotropic: (i) the 2-D stratum between lamellae surfaces (which is on average normal to the fiber axis) constrains the trajectories of folded and "tie" chains, and (ii) the interfibrillar channels and amorphous chains are extended parallel to the fiber axis. These interlamellar and interfibrillar regions are expected to transform as the fibers are drawn. Hence a probe molecule ($D_2O$) diffusing in this complex amorphous topology would be expected to acquire some net orientational order which due to the fiber geometry is axial in nature and sensitive to the draw ratio. This residual probe anisotropy can be conveniently measured with $^2$H NMR.[10−12] Ideally, for water that is restricted to a homogeneous anisotropic domain (with rapid diffusion and deuteron exchange), a quadrupolar splitting $\Delta\nu$ is observed which is directly related to the O−D bond order parameter, $\langle P_2(\cos\theta)\rangle = \langle(3\cos^2\theta - 1)/2\rangle$, where $\theta$ is the instantaneous orientation of the O−D bond relative to the dominant direction of the motional constraints in the domain and the brackets indicate a time average. The constraint direction is identified as the local symmetry axis or the local director **n**. A non-zero-order parameter indicates that the O−D bond direction is incompletely averaged by anisotropic molecular motion. In fluid media this residual probe orientation is related to $\Delta\nu$ by[8,10−12]

$$\Delta\nu = 2\nu_q\left[\langle P_2(\cos\theta)\rangle + \frac{1}{2}\eta\langle\sin^2\theta\cos 2\phi\rangle\right]P_2(\cos\Omega) \quad (1)$$

where the quadrupolar interaction constant $\nu_q = {}^3/_4(e^2qQ/h)$ (≅160 kHz for the O−D bonds in water[6,7,13,14]) and $\theta$ and $\phi$ are the instantaneous polar and azimuthal angles between the O−D bond and the local director; **n** is assumed to be coincident with the fiber axis. The asymmetry parameter $\eta$ characterizes the electronic distribution in the probe molecule and specifies the asymmetry of the static electric field gradient tensor at the deuteron ($\eta \cong 0.1$ for O−D bonds[6,13,14]). $\Omega$ is the angle between the director and the magnetic field direction, **H**. For the uniaxial system studied here, changing the fiber axis relative to **H** yields spectra wherein $\Delta\nu$ varies as the second Legendre polynomial $P_2(\cos\Omega)$. The utility and sensitivity of $^2$H NMR as an indicator of residual motional anisotropy stems from the

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

S0024-9297(95)01484-7 CCC: $12.00 

fact that in liquid-like phases, NMR spectroscopy enables one to determine readily very small $\Delta\nu$'s (on the order of 1 Hz). Therefore, according to eq 1, order parameters $\langle P_2(\cos\theta)\rangle$ as small as $10^{-5}$ can be detected; i.e., very subtle departures from isotropy can be determined.

In the amorphous matrix of the nylon fibers, the $D_2O$ molecule probes different anisotropic environments and will exhibit $\Delta\nu$ values which reflect a complex weighted average of order parameters which is related to the probe residence time in the variety of different constraints, e.g., interlamellar versus interfibrillar constraints, temporary residence on orientationally restricted amide groups, etc. Here we report the dependence of $\Delta\nu$ on $D_2O$ concentration, temperature, and draw ratio of the fibers. The line shapes for partially exchanged N−D bonds in dry fibers is also reported. We attempt to relate the NMR findings to the earlier SANS data[1] in order to construct a more detailed picture of the morphology in nylon 6 fibers.

## Experimental Procedure

**Sample Preparation.** Undrawn (1.0×) and drawn (2.5, 3.0, 3.5, 4.0, and 4.5×) round cross section nylon 6 fibers used in this study are the same as those used in the earlier SANS work.[1] The fibers were drawn hot; the roll temperature was 175 °C and the pin temperature was 75 °C. Prior to use, the fibers were dried under vacuum at 100 °C for 24 h and stored in a desiccator.

The fibers were hydrated (~6 wt % $D_2O$) by immersion in liquid $D_2O$ for at least 2 h (past the fiber saturation limit). Hydrated fiber samples for NMR measurements were prepared by first patting the wet fibers dry (to remove superficial $D_2O$) and then pulling bundles of quasiparallel fibers through a conventional melting point capillary tube (1.5−1.8 mm o.d.). The fibers were thus maintained in a tightly packed, parallel arrangement with respect to each other and the tube axis. The capillary tubes were sealed with Parafilm. With this configuration, angular (Ω) dependent NMR measurements could be made by inserting the capillary between the turns of an 8 mm transverse, solenoid rf coil of variable pitch (it was stretched apart in the center to accommodate the 1 mm capillary) and by varying the angle (Ω) between the capillary tube axis and **H**. Each of these samples contained ~50 mg of hydrated fibers.

Dry (deuteron exchanged) fibers were prepared by immersing the fibers in $D_2O$ for 12 h and then drying them under vacuum for 12 h. The dry fiber samples for Ω-dependent NMR measurements were arranged in three different configurations: (i) $\Omega = 0°$ (fiber axis parallel to **H**), (ii) $\Omega = 90°$ (fiber axis perpendicular to **H**), and (iii) powder (random Ω distribution). (Due to the smaller amount of deuterium in these dry fibers, a different configuration than the one described above for the hydrated fibers was used to accommodate a larger amount of sample.) In order to align the fiber axes with $\Omega = 0°$ in the transverse solenoid coil, we tightly wrapped a bundle of the dry fibers (~6 mm in length) parallel to one another in Parafilm and then placed the wrapped bundle in a conventional 8 mm NMR tube such that the mean fiber axis direction was perpendicular to the NMR tube axis. Due to the poor filling factor of fibers in the NMR coil with this arrangement (only ~100 mg of fibers was situated in the NMR tube), larger samples for $\Omega = 90°$ measurements were prepared by pulling ~1 g of the fibers through a conventional 5 mm NMR tube such that the fiber bundles were tightly packed parallel with respect to each other and the tube axis. The powder sample was prepared by cutting the fibers into 1−5 mm in length segments and filling an 8 mm NMR tube with ~300 mg of the randomly aligned segments. All of the sample tubes were sealed with Parafilm.

**NMR Measurements.** Solid-state NMR measurements on both the hydrated and dry fibers were made with a Bruker MSL-360 spectrometer (55.48 MHz) using a high-power transverse 8 mm rf coil (except for the $\Omega = 90°$ measurements of the dry fibers, where a 5 mm rf coil was used). For the acquisition of all spectra, a quadrupolar echo pulse sequence ($[90°x-\tau_1-90°y-\tau_2-T_d]$) was used with a 90° pulse width between 2.2 and 2.6 μs (2.0 μs for the 5 mm unstretched rf coil), a recycle delay time $T_d = 1.0$ s, and $\tau_1$ and $\tau_1$ varied between 15 and 17 ms. Sweep widths of 40 kHz were used for measurements of the hydrated fibers and sweep widths of 400 kHz were used for the broad-line measurements of the dry fibers. An inversion−recovery pulse sequence ($[180°x-\tau-90°x-T_d]_n$) with quadrupolar echo pulse detection was used for the $T_1$ measurements of both the hydrated and dry fibers with a 90° pulse width of 2.2 μs for the hydrated fibers and 2.0 μs for the dry fibers and a delay time of 1 s for one cycle ($n = 1$). Relaxation times were determined from a two-variable (the equilibrium value of the magnetization vector along the $z$ axis ($M_{z0}$) and the spin−lattice relaxation time ($T_1$)) fit of signal intensity vs $\tau$ values.

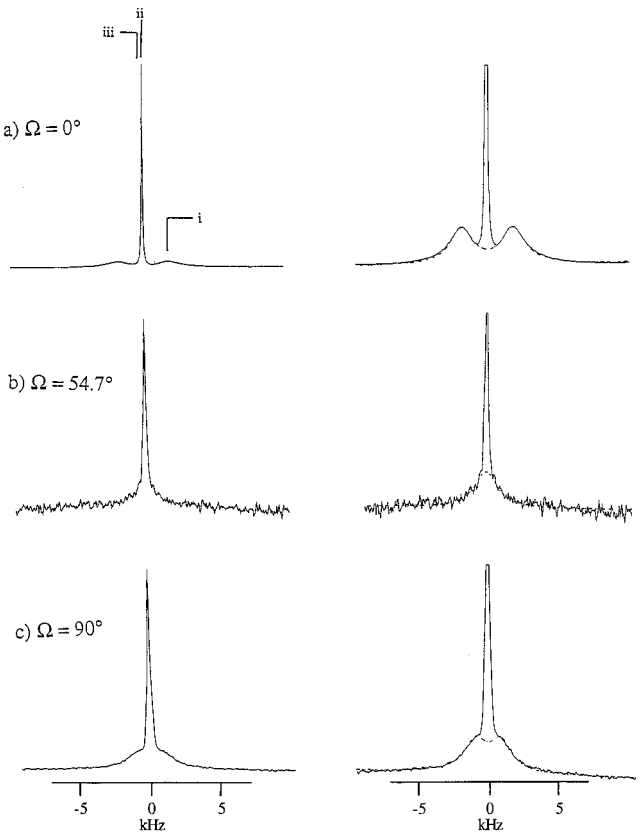


**Figure 1.** Angular-dependent $^2H$ NMR spectra of hydrated nylon fibers (~6 wt % $D_2O$; draw ratio 4.5×); Ω corresponds to the angle between the fiber axis and the magnetic field of the spectrometer. The simulated quadrupolar splittings are shown as dashed lines underneath the experimental spectra which are magnified in the right panel. The markers i, ii, and iii indicate the frequencies at which $T_1$ measurements were performed on the 4.5× fiber ($\Omega = 0°$). The fiber has apparent $T_1$ values which are dependent upon resonance position where $T_1$(i) = 0.003 s, $T_1$(ii) = 0.150 s, and $T_1$(iii) = 0.200 s.

## Results and Discussion

**Angular Dependence of $^2H$ NMR Spectra of $D_2O$.** Figure 1 shows the experimental $^2H$ NMR spectra of the 4.5× drawn nylon fibers at different fiber axis orientations: $\Omega = 0°$, $\Omega = 54.7°$, and $\Omega = 90°$. In the $\Omega = 0°$ orientation (fiber axis parallel to the field), the spectrum consists of a narrow central resonance with a full-width at half-height (FWHH) line width $\Gamma(\Omega{=}0°) = 50$ Hz superimposed on a lower intensity, broad doublet with a FWHH $\Gamma'(\Omega{=}0°) \sim 1500$ Hz and a splitting of $\Delta\nu(\Omega{=}0°) = 3420$ Hz. At the "magic angle",

$\Omega = 54.7°$, $P_2(\cos \Omega) = 0$ in eq 1 and the broad resonances (residual quadrupolar interactions) disappear (Figure 1b); the $\Omega = 55°$ singlet FWHH $\Gamma(\Omega=55°) = 200$ Hz. At $\Omega = 90°$ the FWHH line widths of both components of the spectrum are reduced by a factor of 2 relative to the $\Omega = 0°$ spectrum (Figure 1c). Since the broad doublet in Figure 1a varies as $P_2(\cos \Omega)$, it can be attributed to a partially resolved quadrupolar splitting. Moreover, the fact that the doublet FWHH $\Gamma'(\Omega=90°) = 1/2\Gamma'(\Omega=0°)$ implies that the inherent line width of the quadrupolar doublet may be the result of a superposition of unresolved quadrupolar splittings; i.e., the doublets are inhomogeneously broadened resonances.

The observed spectra and the reported quadrupolar splittings were simulated at all three orientations ($\Omega = 0°$, $\Omega = 54.7°$, and $\Omega = 90°$) with single Lorentzian lines and could not be differentiated from simulations based on a superposition of narrow doublets with splittings and intensities distributed in a Guassian manner about the mean splitting, $\Delta\nu(\Omega=0°)$. The best fit, determined by qualitatively superposing the experimental and simulated spectra, was achieved for $\Delta\nu_s(\Omega=0°) = 3500$ Hz and $\Gamma'_s(\Omega=0°) = 1840$ Hz. The simulations are shown as dashed lines overlapping the magnified experimental spectra (right side of Figure 1). The simulated value for the quadrupolar splitting at $\Delta\nu_s(\Omega=0°) = 3500$ Hz is marginally greater than the value measured as the frequency difference between the apparent center of the two broad resonances ($\Delta\nu(\Omega=0°) = 3420$ Hz).

**$^2$H NMR Spectra of $D_2O$ vs Fiber Draw Ratio.** A quadrupolar splitting is evidence for residual orientational order for a fraction of the $D_2O$ in the nylon fibers. The fact that the observed $\Delta\nu(\Omega=0°)$ is approximately 1% of the maximum static value ($\Delta\nu = 250$ kHz) indicates that there is significant motional averaging of the quadrupolar interaction by (exchange-mediated) diffusion of the water in the hydrated nylon. Figure 2 shows $\Omega = 0°$ spectra of hydrated nylon fibers as a function of fiber draw ratio. At all draw ratios, the spectrum consists of a narrow "isotropic" resonance superimposed on a broad quadrupolar doublet. The broad doublet exhibits an apparent linear dependence of the observed quadrupolar splitting on the draw ratio (Figure 3) where the magnitude of $\Delta\nu(\Omega=0°)$ increases with draw ratio. This is evidence that the orientational order in that fraction of the $D_2O$ exhibiting the doublet increases with draw ratio. This could be a reflection of improved alignment within ordered domains, increased relative ordering of the domain directors, and/or a change in the averaging process (interdomain diffusion) of this water. By correlating the changes in the spectra shown in Figure 2 on partially drying the hydrated nylon (see below) with the SANS findings,[1] we are compelled to associate the broad doublet with $D_2O$ in the interfibrillar channels. And, as the anisotropy of these channels is observed to increase with draw ratio—the channel lengths increase from about 1500 to 2000 Å upon drawing from 1.0× to 4.5× according to the SANS measurements[1]—it is reasonable to expect that the motional averaging of the quadrupolar interaction would become even less effective, corresponding to an increase in $\Delta\nu$ with fiber draw ratio.

On closer inspection, the angular dependence of the "isotropic" component of the spectra in Figure 1 is disconcerting: At $\Omega = 0°$ the central resonance has a FWHH line width of ~110 Hz but at $\Omega = 90°$ this line width *broadens* to ~220 Hz. This is again illustrated in Figure 4, which shows the $^2$H NMR spectra of the hydrated 4.5× fibers which were partially dried (under vacuum for a total of approximately 30 min). Drying

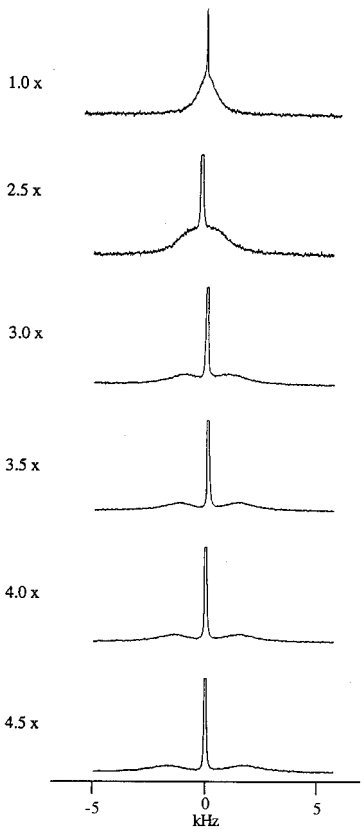


**Figure 2.** $^2$H NMR spectra of aligned, hydrated nylon fibers (5−10 wt % $D_2O$) as a function of draw ratio where 1.0× corresponds to the undrawn (as spun) fiber, $\Omega = 0°$. The spectra are shown at 10× normal intensity.

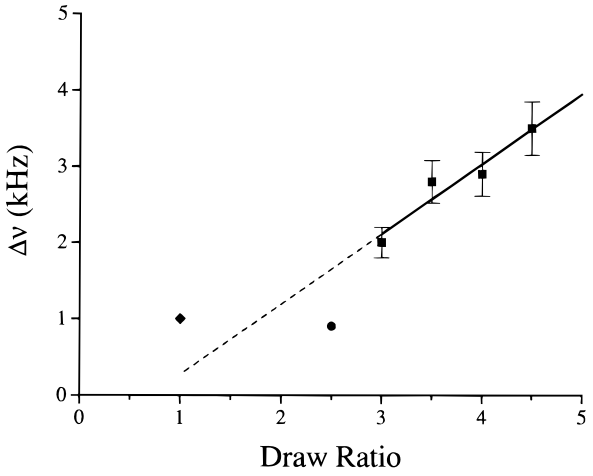


**Figure 3.** Apparent quadrupolar splitting $\Delta\nu$ (kHz) versus draw ratio of nylon fibers ($\Omega = 0°$). /bsd represents experimental $\Delta\nu$ values which were measured as the frequency difference between the apparent centers of the quadrupolar resonances for the 3.0−4.5× drawn fibers (see Figure 1). The linear fit of these values is indicated by the solid line, and the extrapolation of this line to draw ratio 1.0× is shown as the dashed line. Estimated values of $\Delta\nu$ for the 1.0× (♦) and 2.5× (●) draw fibers (which are unresolved in Figure 1) are also included. The value of $\Delta\nu$ for the 1.0× fiber was estimated from the resolved quadrupolar splitting observed in the $^2$H NMR spectra of partially dried fibers at $T = 330$ K (see Figure 6a). The $\Delta\nu$ value corresponding to the 2.5× draw fiber was derived from simulations (as described in the text) of the experimental $^2$H NMR spectra.

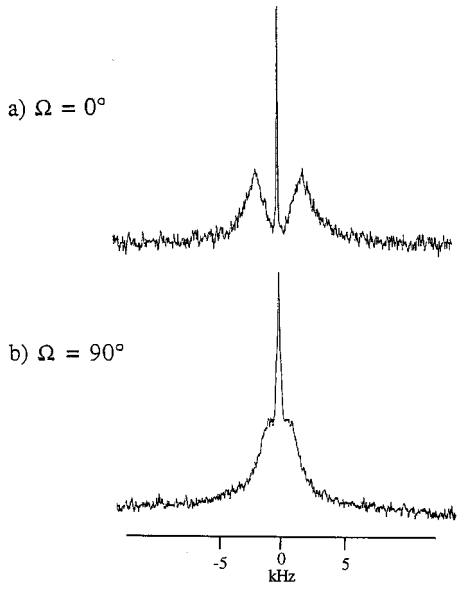


**Figure 4.** $^2$H NMR spectra of 4.5× drawn nylon fibers hydrated with $D_2O$ at orientations (a) $\Omega = 0°$ and (b) $\Omega = 90°$. The fibers were periodically dried under vacuum for a total of ~30 min.

the fibers removes a portion of the $D_2O$ that contributes to the central resonance. At $\Omega = 0°$, the central peak is still sharp in the partially dried fibers, with a FWHH line width of $\Gamma(\nu) \sim 145$ Hz. At $\Omega = 90°$, the central peak is no longer a single isotropic resonance but is a superposition of an unchanged central (isotropic) resonance (with $\Gamma(\nu) \sim 145$ Hz) on a much broader resonance. If we assume that this broader resonance is an unresolved quadrupolar doublet with $\Delta\nu(\Omega{=}90°) \approx 970$ Hz (having a shifted center of gravity), then we would expect to see a doublet $\Delta\nu(\Omega{=}0°) = 2\Delta\nu(\Omega{=}0°)$ when the fibers are parallel to the field. However, such a doublet with a splitting of $\Delta\nu(\Omega{=}0°) \approx 1900$ Hz (and the same shifted center of gravity) is largely obscured by the inner shoulders of the broad quadrupolar doublet in the $\Omega = 0°$ spectrum. This angular dependence of the broad central resonance indicates that two different classes of water molecules (one isotropic and one which may be partially oriented) comprise this component of the spectrum.

**Spin−Lattice Relaxation Times of $D_2O$.** It is apparent from the $^2$H NMR spectra of the hydrated nylon fibers (Figures 1, 2, and 4) that the $D_2O$ molecules experience as many as three different environments—the anisotropic environments which exhibit a broad quadrupolar splitting and a sharper doublet (Figure 4) and a nearly isotropic environment (the central resonances). In an effort to further delineate the differences between these three types of water, we examined the $T_1$ values of $D_2O$ in the drawn fiber (4.5×) with $\Omega = 0°$. The measured $T_1$ value of the quadrupolar splitting, $T_1(\text{i}) = 0.003 \pm 0.001$ s, is much shorter than those $T_1$ values determined for the central resonances, $T_1(\text{ii}) = 0.150 \pm 0.006$ and $T_1(\text{iii}) = 0.207 \pm 0.002$ s. (The frequencies at which these $T_1$ values were evaluated are indicated in Figure 1a.) The relaxation times of the central component, $T_1$(ii) and $T_1$(iii), are shorter than those for $D_2O$ in wet hydrated fibers, $T_1 = 0.370$ s (which approximates that for pure liquid $D_2O$, $T_1 = 0.400$ s). This indicates that the central resonance components are dynamically different from superficial $D_2O$.

**$^2$H NMR Spectra of $D_2O$ vs Drying Time.** In a further attempt to eliminate contributions to the spectrum from superficial water and isotropically bound water, the 1.0× and 4.5× hydrated fibers were dried (in unsealed tubes) under atmospheric conditions at 310 K. The $^2$H NMR spectra with $\Omega = 0°$ as a function of drying time are shown in Figure 5. At both draw ratios, the central resonances disappear first, leaving a broad quadrupolar doublet. The intensity of the doublet in both fibers decreases slightly with the initial drying time (it eventually disappears on prolonged drying) while the magnitude of the splitting remains essentially constant. This indicates that, in constrast, to the "isotropic" $D_2O$, the anisotropic $D_2O$ is more strongly bound and maintains the same average degree of order during drying. Figure 5a also indicates that the broad resonance observed for the 1.0× fiber in Figure 1a is in fact comprised of an unresolved quadrupolar doublet (filled triangle in Figure 3).

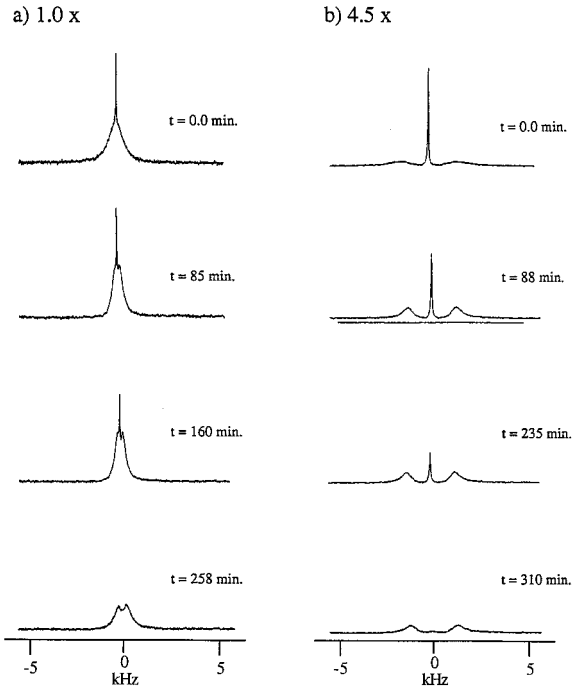


**Figure 5.** Evolution of $^2$H NMR spectra of hydrated nylon fibers (4.5×) versus drying time; the central ("isotropic") resonance disappears first when the fibers are heated under atmospheric conditions at 310 K.

**$^2$H NMR Spectra of $D_2O$ vs Temperature.** The magnitudes of $\Delta\nu$ for the 1.0× and 4.5× dried samples at $\Omega = 0°$ are shown as a function of temperature in Figure 6. The FWHH line widths of the anisotropic resonances (for both the 1.0× and 4.5× fibers) decrease with increasing temperature. The magnitude of the quadrupolar splitting associated with the 1.0× fibers remains essentially constant (Figure 6a) while that of the 4.5× fibers decreases with increasing temperature (Figure 6b). The temperature dependence of the NMR spectra of these partially dried fibers is suggestive of a thermally activated process wherein the average anisotropy of the water becomes better defined at elevated temperatures. This process might involve both chemical exchange (of deuterons with accessible amides that are motionally restricted) and anisotropic reorientational motions of the $D_2O$ (in confined spaces—interfibrillar channels and interlamellar cavities). In the case of the water in the 1.0× fibers, the average anisotropy would appear to remain constant over the temperature range examined ($\Delta\nu(\Omega{=}0°) \cong 1$ kHz). The behavior in the 4.5× fiber is qualitatively different. As discussed

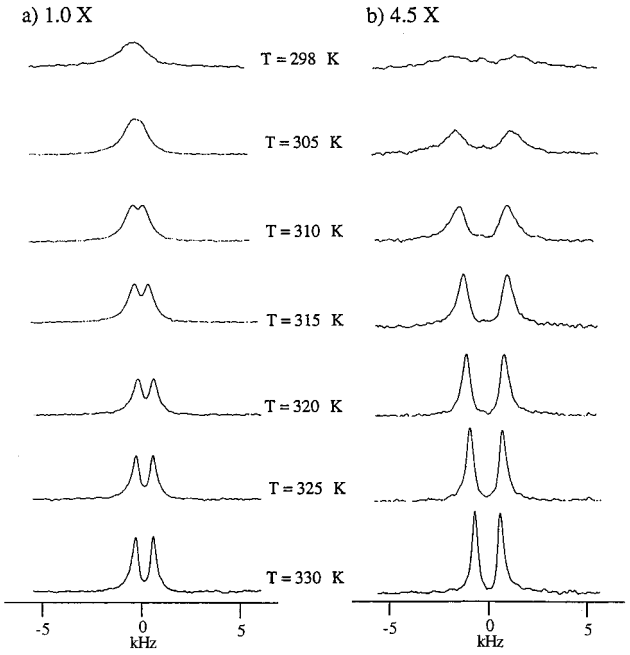


**Figure 6.** $^2$H NMR spectra of oriented $D_2O$ in (a) 1.0× and (b) 4.5× nylon fibers versus temperature ($\Omega = 0°$).

earlier, the angular dependence (Figure 1) of the broad doublet in the 4.5× fiber (Figure 6b; $\Delta\nu_s(\Omega{=}0°) = 3.5$ kHz at 298 K) is indicative of a superposition of anisotropic averages distributed in an approximate Gaussian manner about some mean value. Figure 6b shows that heating the fiber by a mere 10° sharpens this distribution. On further heating, it is clear that the magnitude of the increasingly better defined mean quadrupolar interaction is decreasing. At 330 K $\Delta\nu$-$(\Omega{=}0°) \cong 1.5$ kHz, a factor of about 2 decrease in degree of order over a ~30° temperature range. This behavior suggests that perhaps in addition to an increased sampling range (faster self-diffusion of the $D_2O$), the intrinsic anisotropy of the sites sampled by the $D_2O$ decreases as the temperature is varied; i.e., there is increased motion of those chains having accessible amide exchange sites and the contour of the channels becomes more convoluted as the morphology begins to soften.

**$^2$H NMR Spectra of Dry (Deuteron Exchanged) Nylon Fibers.** When the hydrated 4.5× fiber is studied at higher spectral widths, the $\Omega = 90°$ spectrum shows, in addition to the broad doublet (unresolved central feature at $\nu = 0$ kHz in Figure 7a), two broad shoulders appear at ±50 and ±75 kHz. The unresolved central doublet disappears when fibers are dried under vacuum (Figure 7b). The residual broad powder-like features in Figure 7b can be attributed to deuterium-exchanged amide groups. Deuteron exchange with accessible N−H groups of nylon has been identified previously with infrared[3] and NMR[4] spectroscopy. The draw ratio dependence of the N−D powder spectra of dried fibers is complex (Figure 8): At $\Omega = 90°$ there is essentially no change in the powder spectra with draw ratio. However, at $\Omega = 0°$ there is the clear emergence of a sharp quadrupolar doublet (±60 kHz) from the broad powder-like background with increasing draw ratio. This sharp doublet is evidence for a unique N−D bond orientation relative to the fiber axis in a fraction of the labeled polymer. This uniquely oriented fraction increases with draw ratio.

In an attempt to qualitatively model the observations in Figure 8, we made some simple starting assumptions

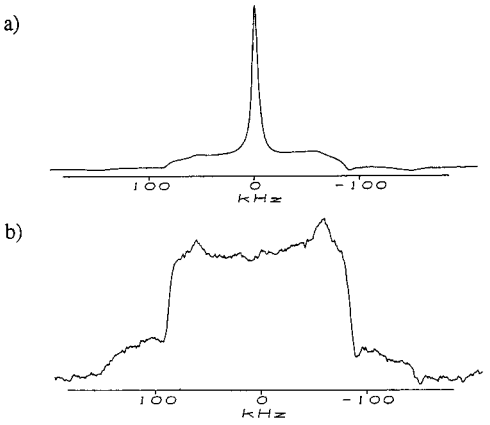


**Figure 7.** Broad-line $^2$H NMR spectra at $\Omega = 90°$ of 4.5× nylon fibers (a) hydrated at ~6 wt % $D_2O$ and (b) after drying in a vacuum oven for 12 h. The $^2$H NMR spectra of the partially dried fibers indicate deuterium exchange on accessible amide groups.

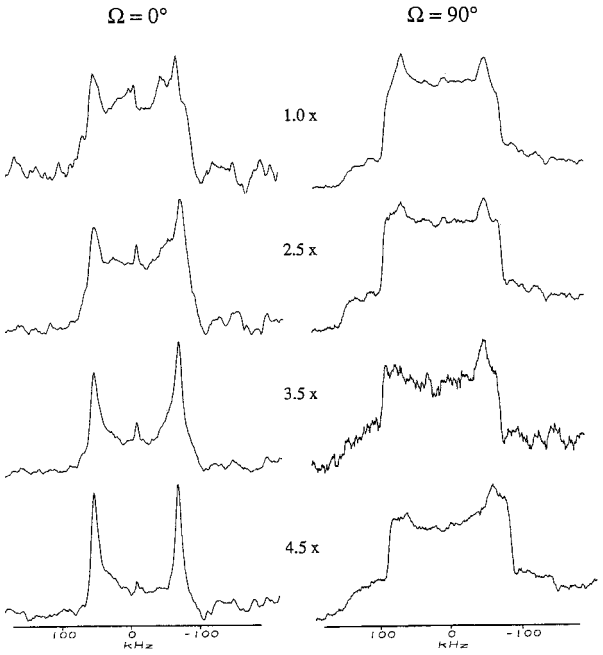


**Figure 8.** Broad-line $^2$H NMR spectra of exchanged N−D bonds in dry nylon fibers (draw ratios: 1.0×, 2.5×, 3.5×, and 4.5×) at $\Omega = 0°$ and $\Omega = 90°$.

consistent with the dominant features of the spectra: (i) the N−H groups with the largest propensity for deuterium exchange reside on amorphous chains; (ii) with the exception of chain folds on crystal lamellae surfaces (and N−H groups on crystal faces), interfibrillar amorphous chains are aligned parallel to the (high draw ratio) fiber axis—the labeled N−H bond vectors will be nearly normal to the fiber axis; (iii) there is undoubtedly chain misalignment (due to inherent disorder of the interfibrillar chains and imperfect fiber alignment in the multifiber bundles). In the simulations of the 4.5× spectrum (Figure 9d−f), the chain misalignment was approximated by a Gaussian distribution of chain axes about the mean fiber axis direction. This chain misalignment in turn introduces a spread of the N−D bond vector orientations about the fiber normal (assumption ii). The width of the Gaussian angular spread ($\beta$) will determine the simulated width of the prominent doublet in the $\Omega = 0°$ spectrum (Figure 9d) as well as the shape of the features in the 2-D powder-like spectrum originating from an azimuthally

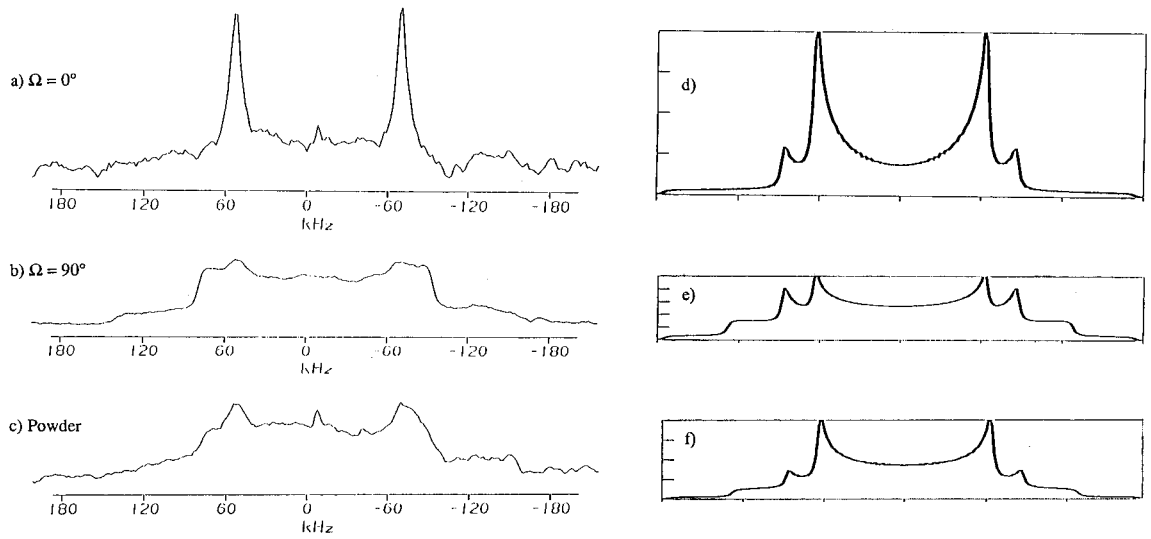


**Figure 9.** Broad-line $^2$H NMR spectra of dry (deuteron exchanged) nylon fibers (draw ratio 4.5×) at orientations (a) $\Omega = 0°$ and (b) $\Omega = 90°$, and (c) a random fiber axis distribution (powder). The spectra are plotted with constant integration. The corresponding simulated $^2$H NMR spectra are also shown in (d) $\Omega = 0°$, (e) $\Omega = 90°$, and (f) powder orientations. Spectra were simulated for 25% of type I deuterons (isotropically distributed with $\nu_q = 232$ kHz and $\eta = 0.0$) combined with 75% of type II deuterons (aligned N−D orientation distribution with $\nu_q = 171$ kHz, $\eta = 0.0$, and $\beta = 20°$).

distributed array of N−D bond vectors normal to the fiber in the $\Omega = 90°$ orientation (Figure 9e). These alignment details are irrelevant in the simulated isotropic powder spectrum (Figure 9f). Additional parameters associated with the simulations are the values for $\nu_q$ and $\eta$, which for nylon range from $\eta = 0.13-0.2$ and $\nu_q = 180-195$ kHz.[4,15,16]

All three experimental spectra of the 4.5× fiber ($\Omega = 0°$, $\Omega = 90°$, and isotropic powder; Figure 9a−c) could not be even qualitatively simulated with any reasonable combination of $\nu_q$, $\eta$, and $\beta$ values. It is necessary to assume at least two different categories of quadrupolar interactions—isotropically distributed N−D bond vectors denoted I and partially aligned bonds, category II—in order to even get very coarse agreement with experiment. In the simulations shown in Figure 9d,e, 25% of type I deuterons (isotropically distributed with $\nu_q = 232$ kHz, $\eta = 0$) is combined with 75% of type II ($\nu_q = 171$ kHz, $\eta = 0$, and $\beta = 20°$). While it does not seem reasonable to assume $\eta = 0$ in view of prior studies,[4,15−19] even this parameter is problematic at this coarse level of simulation. For example, the partially aligned fraction II reasonably accounts for the observed prominent splitting in Figure 9a, where $\Delta\nu(\Omega=0°) = 120$ kHz corresponds to the N−D bonds being on average perpendicular to the field. But the misalignment of chains[20] (a Gaussian spread of $\beta = 20°$) required to approximate the width of these features would give a complex line shape in the simulation if $n \neq 0$. Unable to get a satisfactory simulation of the angular dependence of the 4.5× powder spectra, we attempted to determine if the postulated categories of N−D bonds I and II could be dynamically differentiated. We examined the $T_1$ characteristics of the spectrum of the 4.0× drawn fibers at $\Omega = 90°$ via an inversion−recovery experiment. The stack plot shown in Figure 10 demonstrates that features of the $\Omega = 90°$ spectrum which we identified with these two different N−D types in fact have very similar spin−lattice relaxation rates ($T_1(I) = 0.15 \pm 0.01$ s and $T_1(II) = 0.20 \pm 0.01$ s). Thus the qualitative features of the spectra in Figure 9a−c may have their origin in more subtle aspects of intensity weightings derived from N−D librational dynamics on an "intermediate time scale".[21]

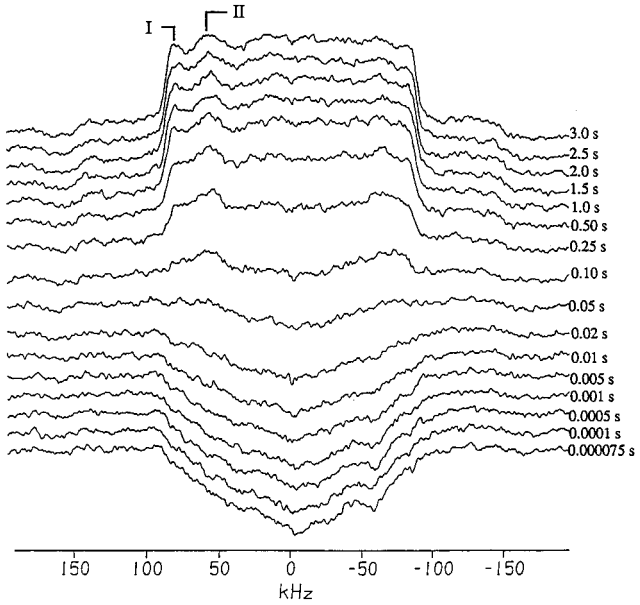


**Figure 10.** Inversion−recovery spectra of dry (deuteron exchanged) 4.0× drawn nylon fibers; $\Omega = 90°$. The resonances corresponding to isotropic type I deuterons (I) have an apparent $T_1(I) = 0.20 \pm 0.01$ s and those corresponding to aligned type II deuterons (II) have an apparent $T_1(II) = 0.14 \pm 0.01$ s.

## Conclusions

We have identified up to three types of water in hydrated nylon 6 fibers—isotropic water and two classes of water with different amounts of draw-ratio-dependent residual orientational order. The water molecules which exhibit the largest anisotropy are strongly bound and are only removed by drying under vacuum. It would appear from the earlier SANS experiments[1] that this bound water resides in interfibrillar channels. By further analogy with the SANS identification of the hydration water, the more readily removable and less anisotropic $D_2O$ is associated with interlamellar regions; the isotropic water is either superficial water or water in macroscopic fiber defects. Solid-state NMR spectra in highly drawn fibers exchanged with $D_2O$ and then dried exhibit a draw ratio dependence. The details of the morphology of the exchanged amides remains

obscure but are generally consistent with the dominent contribution derived from oriented interfibrillar chains and a smaller contribution arising from exchange with variously oriented amide sites on the lamellar fold surface and crystallite faces of semicrystalline nylon.

**Acknowledgment.** We gratefully acknowledge Dr. A. Terzis's help with the preparation of the simulation programs used in this work. This work was supported by National Science Foundation Grant DMR 9412701.

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MA9514840