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Deuterium nuclear magnetic resonance of deuterium oxide in nylon 6 under active uniaxial deformation

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Abstract

The large strain uniaxial tensile deformation behavior of nylon 6 plasticized by deuterium oxide is investigated by an in situ stretching device built in a deuterium nuclear magnetic resonance (NMR) probe. The D_2O molecules probe the environment of the amorphous regions in nylon 6; they do not exist in a "free" state and remain associated with the amide groups by hydrogen bonding during deformation. Deuterium NMR spectra show that the quadrupolar splitting varies linearly with strain throughout the experiment, indicating that the orientation of the D_2O molecules in the amorphous regions is simply a function of strain and not of stress. The line width increases rapidly with strain at low to moderate strains but more slowly at large strains (in the strain-hardening regime). From low to moderate strains, larger changes in line width arise from a decrease in the translational motion of the D_2O molecules between amide groups in the amorphous chains during elastic deformation and during the transformation of the lamellar structure of nylon 6 to a fibrillar one. At large strains, the existence and deformation of the fibrillar structure cause a slower decrease in the translational motion of the plasticizer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Deuterium NMR; Nylon 6; Tensile deformation

1. Introduction

Polyamides are important engineering plastics whose mechanical properties are greatly influenced by its moisture content. Water plasticizes the nylon matrix and causes a reduction in the glass transition temperature (T_g) and Young's modulus [1–3] but enhances the toughening behavior [4]. It was postulated that such behavior is due to the "softening" of the polymer as water disrupts hydrogen bonds between amide groups [1], but to date there has been no work which is able to shed light upon the motional states of the water molecules or polymer chains during deformation.

Extensive evidence has shown that water only penetrates into the amorphous regions of nylon [5–7], but there has been some debate regarding its nature. Puffr and Sabenda have suggested the presence of both "loosely" and "tightly" bound water molecules in the matrix [8]. Using deuterium NMR techniques, we have demonstrated that water molecules exist only in one state in wet nylon [9], thus supporting the viewpoint held by le Huy and Rault [10].

We intend to continue to utilize this powerful tool to examine the motion of such absorbed water molecules while the polymer is undergoing active deformation, thereby giving insight into the deformation process and the role of the plasticizer. There have been various NMR studies on plasticizers in polymers [11–13]. The amount of experimental data available on actively deforming polymers is limited. In an earlier work we studied phenol-d_5 in deforming nylon 6, the former being chosen because it does not undergo exchange with the hydrogen atom on the NH group and because of the resulting good signal to noise since it is absorbed in large quantities [14]. Other researchers have also used deuterium NMR to investigate small strain deformation in deuterated polycarbonate [15] and performed time resolved simultaneous X-ray of polyethylene undergoing active cold drawing [16].

2. Materials and methods

Two millimetre diameter nylon 6 rods were purchased from Goodfellow Corporation and deuterium oxide was obtained from Cambridge Isotope Laboratories. The molecular weight of the polyamide is 60,000 g/mol, determined from viscometry measurements using 2,2,2-trifluoroethanol as a

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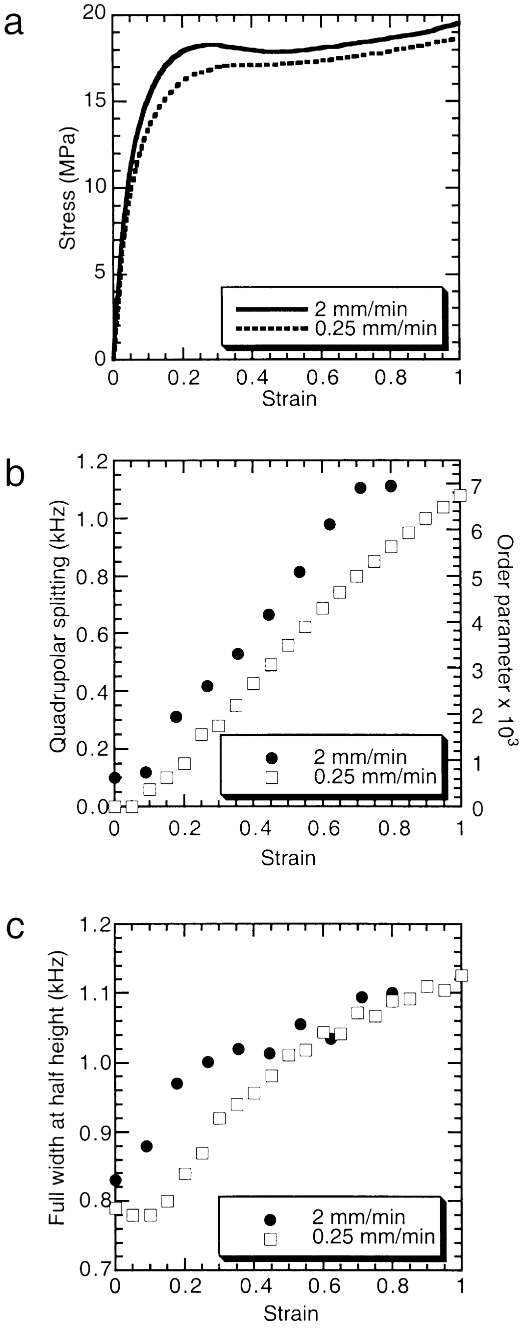

Fig. 1. (a) Stress–strain curve of nylon 6 rod plasticized with D_2O at elongation rates of 2 and 0.25 mm/min. (b) Quadrupolar splitting (kHz) versus strain. (c) Line width (kHz) versus strain.

solvent at 23.5 ± 0.5°C. Differential scanning calorimetry (DSC) showed that the crystallinity of the material is about 30%. Without any further modification the rods were dried in vacuum at 100°C for 48 h to remove trace water. The rods were then immersed in D_2O until equilibrium was achieved, which took about a month. Equilibrium was considered attained when no weight change was recorded on successive days. These rods were then subsequently used in Instron and NMR experiments.

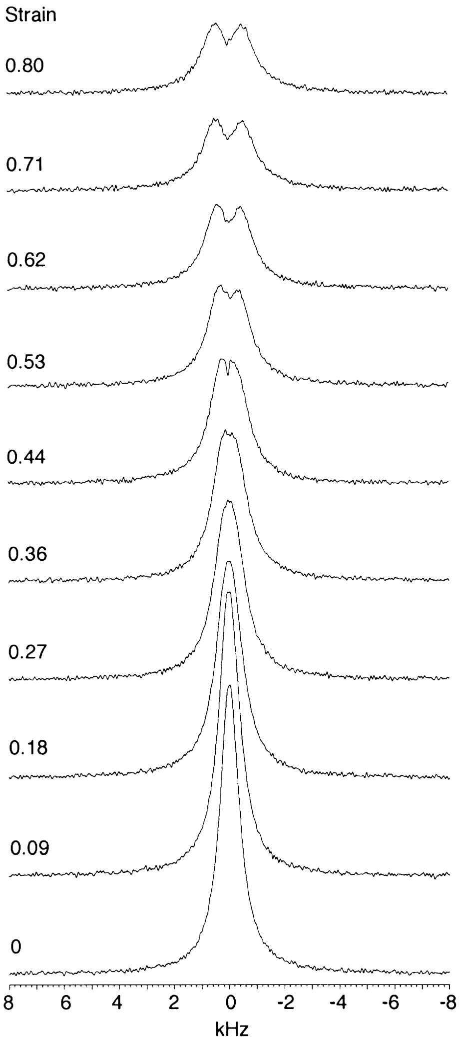

Fig. 2. Deuterium NMR spectra of D_2O in nylon 6 rod undergoing active tensile deformation. The corresponding strains are shown on the left. The elongation rate is 2 mm/min. Each spectra is the accumulation of 300 scans with a digitization rate of 20 μs.

The uniaxial tensile experiments were performed on an Instron 4201 machine to obtain the stress–strain curves. The gauge length of the samples was 10 mm and they were stretched to lengths of 20 and 18 mm at elongation rates of 0.25 and 2 mm/min, respectively. Over the time scale of the experiments, typically less than 1 h, there was negligible loss of D_2O molecules to the atmosphere, as determined by simply placing a control sample on the machine and measuring its weight an hour later.

The NMR work was done at room temperature at 45.8 MHz for deuterium. A stretching device was constructed in a deuterium NMR probe to perform in situ uniaxial tensile experiments [14]. The 90° pulse time was 5.4 μs. Free induction decays (FID) were obtained by using a single 90° pulse. The recycle delay was 0.1 s and the digitization rate used was 20 μs with a total acquisition time of 10.24 ms. In the experiments with elongation rates

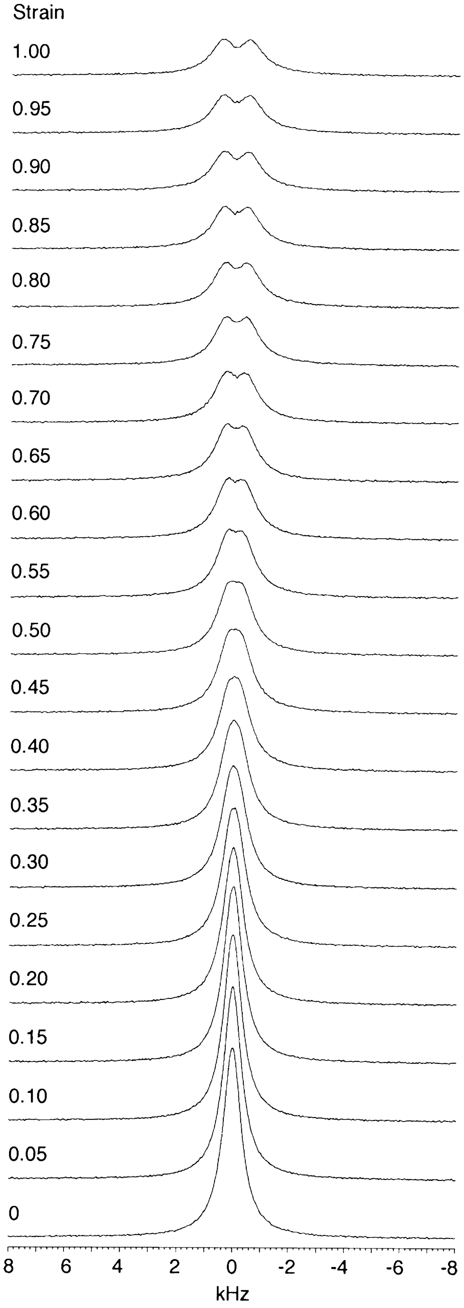

Fig. 3. Deuterium NMR spectra of D_2O in nylon 6 rod undergoing active tensile deformation. The corresponding strains are shown on the left. The elongation rate is 0.25 mm/min. Each spectra is the accumulation of 1200 scans with a digitization rate of 20 μs.

of 2 and 0.25 mm/min, 300 and 1200 scans, respectively, were needed for each spectrum.

3. Results and discussion

Fig. 1a shows plots of engineering stress versus engineering strain (strain, ε, is defined as $\varepsilon = \Delta L/L_0$ where ΔL is the increase in length and L_0 is the initial length of the sample) of nylon 6 which is fully saturated with D_2O (i.e. gained 12 wt% of D_2O). Both curves show a yield point and strain hardening. In addition, the curve for the faster elongation rate exhibits a yield drop. The deformation was homogeneous and necking did not occur in either sample. Plasticization of the amorphous regions of the nylon rods by the D_2O molecules resulted in yield strengths of less than 20 MPa, much lower than that of dry nylon (76 MPa) [4].

Figs. 2 and 3 show two series of deuterium NMR spectra of D_2O molecules in the amorphous phase of nylon 6 as a function of strain for elongation rates of 2 and 0.25 mm/min, respectively. It is known that D_2O molecules undergo chemical exchange with the NH groups in the amorphous regions [5,6]. However, as the exchange rate is slow ($\sim 10^{-5}$ s), it is possible to selectively detect only signals from D_2O (as is the case for Figs. 2 and 3) by using a slow digitization rate (20 μs) during acquisition [9]. The bottommost spectrum of each figure shows the spectrum of D_2O in the undeformed rod. It is a narrow Lorentzian with a line width of less than 850 Hz indicating that the order parameter is zero and that the D_2O molecules in the amorphous regions undergo isotropic reorientation which is fast compared to the quadrupolar interaction (~200 kHz). The line widths of the spectra increase with strain and eventually split into a doublet at higher strains. The samples in the probe deformed in a homogenous manner without necking as in the corresponding Instron experiments.

The narrow line widths throughout Figs. 2 and 3 indicate that, even at large strains, D_2O is still in the motionally narrowed limit. The presence of a doublet in the upper spectra in both Figs. 2 and 3, then, proves that D_2O molecules probing the amorphous regions in the strained nylon have a non-zero order parameter. The NMR spectrum of a deuteron in a small molecule diffusing in an anisotropically ordered medium consists of a doublet whose splitting $\Delta\nu$ is given by [11,12,17,18]

$$\Delta\nu = \frac{3}{2}\nu_q\left[\langle P_2(\cos\theta)\rangle + \frac{1}{2}\eta\langle\sin^2\theta\cos 2\phi\rangle\right]P_2(\cos\Omega) \quad (1)$$

where ν_q is the quadrupolar coupling constant, η the asymmetry parameter, θ and ϕ the instantaneous polar and azimuthal angles between the OD bond and the stretching direction, and Ω the angle between the stretching direction and the magnetic field. The quadrupolar splitting is directly related to the average order parameter $\langle P_2(\cos\theta)\rangle = \langle(3\cos^2\theta - 1)/2\rangle$ of the OD bonds of the D_2O molecules in the amorphous phase. Moreover, in those spectra showing a doublet, no central peak is observed. Thus, there are no "free" (i.e. isotropically mobile as in a liquid, thereby resulting in a narrow central Lorentzian peak [12,19]) D_2O molecules throughout the deformation process. Such a splitting has also been observed for benzene-d_6 in polystyrene solution of a concentration of 125 mg/ml undergoing shear [20] and in the authors' previous work [14] with phenol-d_5 in nylon.

As further proof of the anisotropy of the environment

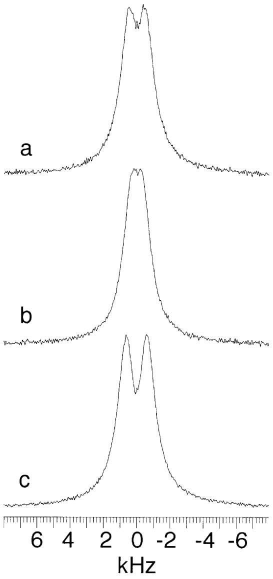

Fig. 4. Deuterium NMR spectra of D_2O in nylon 6 rod with its axis at angles of $\Omega = 0°$ and $\Omega = 90°$ to the magnetic field: (a) at maximum elongation under tension with $\Omega = 90°$, (b) after release from tension with $\Omega = 90°$, (c) after release from tension with $\Omega = 0°$.

probed by the D_2O molecules due to deformation, the polymer sample which was elongated at 2 mm/min, was removed from the probe 4 h after the deformation. The sample contracted as it was released from stress. A section of the deformed specimen was cut and placed in the probe. NMR acquisition was done with the sample axis oriented at angles of $\Omega = 0°$ and $\Omega = 90°$ to the magnetic field. The resulting spectra are shown in Fig. 4b and c. When the sample is still under stress at maximum elongation (Fig. 4a, $\Omega = 90°$), the quadrupolar splitting is 1108 Hz. The effects of the sample being released from stress can be seen by the reduced quadrupolar splitting (722 Hz) in Fig. 4b, the lower value for splitting a result of lower degree of orientation due to chain relaxation. As expected from Eq. (1), the spectra for the relaxed specimen ($\Omega = 0°$) in Fig. 4c shows twice the quadrupolar splitting (1450 Hz) compared to that in Fig. 4b ($\Omega = 90°$), indicating that the D_2O molecules are experiencing an anisotropic environment in the deformed material. By substituting $\nu_q = 213.2$ kHz [21], $\Omega = 90°$ and $\eta = 0$ into Eq. (1), we can calculate the average order parameter $\langle P_2(\cos\theta)\rangle$ of the OD bonds in the amorphous regions along the stretched direction. We have chosen to neglect the small value of the asymmetry parameter ($\eta \sim 0.1$ for OD bonds [21]) in order to get an order of magnitude estimate for the order parameter. The resulting values of $\langle P_2(\cos\theta)\rangle$, which are in the order of 10^{-3}, are shown on the right axis in Fig. 1b and they agree well with the results of Hutchison et al. [11] for D_2O in nylon 6 fibers at low draw ratios. Schreiber et al. have measured the order parameter of the amorphous region in hot drawn nylon 6 fibers using carbon-13 solid state NMR and calculated a value of 0.06 for nylon 6 fibers of draw ratio 2 [22]. The lower time averaged values obtained for D_2O reflects in part the ability of the solvent molecules to sample several sites in the drawn nylon 6 matrix during the NMR measurement period. Furthermore, the order parameters of phenol-d_5 in stretched nylon 6 [14] are four times higher than that of D_2O, implying that the mobility of the bulkier probe molecule is more restricted.

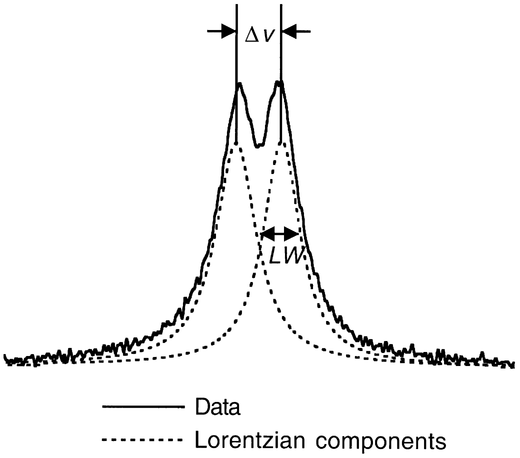

Fig. 5. The deuterium spectrum in Fig. 3 at a strain of 1.0, with the least squares components obtained by regression. The quadrupolar splitting is represented by $\Delta\nu$ and the line width by *LW*.

Each spectrum in Figs. 2 and 3 was regressed using two Lorentzian components as shown in Fig. 5. The distance between the peaks of the two components is taken to be the quadrupolar splitting. Fig. 1b and c shows, respectively, the plots of the quadrupolar splitting and line width (taken as the average of the line widths of the two fitting components) versus strain.

From Fig. 1b, the splitting varies fairly linearly with strain for both elongation rates even though the stress–strain curve shows a non-linear behavior. The splitting shows little deviation from linearity at strains where yield, yield drop and strain hardening are observed. This indicates that the orientation of the D_2O molecules associated with the amorphous chains is a function of strain rather than of stress. The slower elongation rate gives rise to a slightly lower splitting which can be attributed to some relaxation of the polymer chains.

On the other hand, the line width data in Fig. 1c behaves differently. At low and intermediate strains, the line width shows a more rapid increase with increasing strain, whereas at higher strains, the increase is more gradual. This behavior indicates that the mobility of the D_2O molecules in the amorphous regions decreases as the polymer is being elongated. The faster elongation rate results in a higher line width which is due to the more restricted mobility of D_2O in a more oriented environment.

At small strains, the increase in quadrupolar splitting [23] reflects the order of the D_2O molecules associated with the orientation of the amorphous chains as a result of interlamellar shear and other processes that tend to align these chains in the draw direction. The D_2O molecules are sampling a more anisotropic environment which restricts their motion thereby resulting in an increase in line width of the spectra. At the yield point, significant amounts of crystallographic slip in the nylon 6 crystals relieve the constraints on the tie molecules, followed by transformation of the lamellar structure of the crystalline regions to a fibrillar structure during strain softening [16]. The overall effect is to allow the amorphous chains to attain a higher degree of orientation, thereby increasing the quadrupolar splitting and line width of the D_2O spectra.

The subsequent load–extension curve plateau and strain hardening result from the deformation of the fibrillar structure [16]. Though the quadrupolar splitting continues to increase linearly in this region, the increase in line width is more gradual than at small strains. As before, the increase in splitting is attributed to an increase in the orientation of the D_2O molecules directly probing the structural rearrangements of the chains in the amorphous regions as they continue to align along the tensile axis due to deformation. The deformation of the fibrillar structure also restricts the mobility of D_2O resulting in the increase in line width. The results are different from the experiment with phenol-d_5 in nylon where the line width is invariant at high strains.

In order to obtain a better physical picture of the dynamics of the D_2O molecules during deformation, spin–lattice (T_1) relaxation experiments were performed for undeformed nylon 6 rods which had absorbed different amounts of D_2O. The behavior of D_2O in nylon 6 is modeled as both translational reorientation between amide sites and rotational reorientation within individual amide sites [9]. For a spin 1 quadrupole with zero asymmetry parameter, the longitudinal (T_1) and transverse (T_2) relaxation times are related to the spectral densities by:

$$\frac{1}{T_1} = \frac{3\pi^2}{20} v_q^2 \{J_1(\omega_0) + 4J_2(2\omega_0)\} \tag{2}$$

$$\frac{1}{T_2} = \frac{3\pi^2}{40} v_q^2 \{3J_0(0) + 5J_1(\omega_0) + 2J_2(2\omega_0)\} \tag{3}$$

where ω_0 is the Larmor frequency of the deuteron, v_q is the quadrupolar coupling constant of the OD bond, and J_0, J_1 and J_2 are the spectral densities. Due to the short T_1 and T_2 time constants of the samples, spin echo experiments could not be used to measure T_2 directly. The value of T_2^* was taken to be equal to T_2 as field inhomogeneity effects are small. T_2^* is obtained from the line widths of the spectra using the following equation:

$$\frac{1}{T_2^*} = \pi(\text{line width}) \tag{4}$$

If the solvent molecules undergo isotropic reorientation with correlation time τ_c, the spectral densities take on the following forms:

$$J_0 = \tau_c \tag{5}$$

$$J_1 = \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \tag{6}$$

$$J_2 = \frac{\tau_c}{1 + (2\omega_0)^2 \tau_c^2} \tag{7}$$

However, assuming one correlation time alone causes a discrepancy between the T_1 and T_2^* results [9], and Eq. (6) was modified to take into account an additional correlation time τ_T due to translational diffusion [24,25]:

$$J_0 = 2\tau_c + 4\varepsilon^2 \tau_T \tag{8}$$

where ε^2 is the mean square fractional change in the quadrupolar coupling and is assumed to be 1% [25]. The dependence of T_1 on the amount of D_2O absorbed by nylon 6 shows a minimum, indicating correlation times in the order of $\omega_0 \tau_c \sim 1$ [9]. An estimate can be made for the diffusion coefficient, D, using the equation:

$$D = \frac{L^2}{\tau_T} \tag{9}$$

where L is taken to be 8.70 Å which is the distance between consecutive NH groups along a single nylon 6 chain in the α crystal phase [26] and represents an upper limit in the amorphous region.

When the sample is deforming, either or both correlation times should change as the D_2O molecules experience different environments due to structural changes in the polymer. Since the spin–spin relaxation time, T_2, and hence line width are sensitive to slow motions [24], we attribute the behavior of the line width with strain in Fig. 1c to changes in the translational correlation time while the rotational correlation time remains unchanged. In the undeformed sample, the FID time scale of 0.4 ms is longer than that of τ_T which is 0.06 ms [9]. Therefore, one D_2O molecule makes an average of 6 hops between amide sites during the FID. When the polymer is deformed, the line width increases because the frequency of the hops decreases. From Eqs. (3), (4) and (8), the translational correlation time constant τ_T increases with the line width, hence these observations show that the diffusion coefficient decreases with increasing deformation.

As the fibrillar structure is developed at high strains, the D_2O molecules are still able to hop from site to site, albeit with a slower rate than at lower strains. This is in contrast to the results for the bulkier phenol molecules, which can hop between sites in the isotropic nylon matrix but are confined to individual amide sites on the NMR time scale at large strains [14]. The smaller size and hence greater mobility of D_2O compared to phenol-d_5 accounts for this difference.

4. Conclusion

During the active large strain tensile deformation of nylon 6 plasticized by D_2O, the D_2O molecules are found to associate with the amide groups. The quadrupolar splitting varies linearly with strain independent of the rate of elongation. Thus the order parameter of the D_2O molecules is simply a function of strain and not of stress. This is similar to the linear dependence of quadrupolar splitting with draw ratio in the work done by Hutchison et al. on D_2O in nylon 6 fibers [11]. Furthermore, the elongation rate has only a small effect upon the degree of orientation developed. The quadrupolar splitting is reduced once the sample is released from stress indicating relaxation of the polymer chains. The line width of the D_2O spectra increases rapidly with strain at low to moderate strain but more slowly at larger strains. This is attributed to the decrease in the frequency of hops of the D_2O molecules between amide sites as deformation proceeds, and as the morphological texture evolves into a fibrillar structure. This is different from the behavior of the bulkier phenol-d_5 in nylon 6 [14]. Thus deuterium NMR combined with in situ active deformation is a powerful technique to probe the mechanical behavior of plasticized polymers in terms of the orientation developed and the motional states of different plasticizers.

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