Correlation Times of Motion of Deuterium Oxide in Polyamide 6 Rods

Leslie S. Loo, Robert E. Cohen, and Karen K. Gleason*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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ABSTRACT: Deuterium nuclear magnetic resonance (NMR) studies of varying amounts of D_2O absorbed in undrawn commercial polyamide 6 (PA6) rods at room temperature suggest the presence of only one type of water closely associated with amide sites via hydrogen bonding and that its motion can be modeled as both isotropic rotational and translational diffusion. Time constants for spin−lattice relaxation (T_1) and spin−spin relaxation (T_2) are used to obtain correlation times for the motions. The dependence of T_1 on D_2O content shows a minimum, indicating that the correlation time is on the order of $\omega_0\tau_c \sim 1$. Translational diffusion occurs on the time scale of less than 1 ms and describes the motion of D_2O hopping between different solvated sites. The corresponding range of diffusivity of D_2O in PA6, $\sim 10^{-10}$ cm^2/s, agrees with values reported for macroscopic diffusion measurements. Within each solvated site the solvent molecules undergo isotropic reorientation diffusion on the order of nanoseconds. The correlation times of both motions increase with decreasing D_2O content, a trend consistent with plasticization of the polyamide matrix. No evidence is found for "free" water. Solid echo experiments also show that there is slow exchange ($\sim 10^{-5}$ s) between deuterium oxide and the ND bonds of PA6.

Introduction

The mechanical properties of polyamides are influenced greatly by their moisture content, and this has important implications in their use as engineering plastics. Polyamide absorbs water vapor easily from the atmosphere, causing it to be plasticized. At the same time its glass transition temperature (T_g) and Young's modulus are reduced,[1,2] but its toughening behavior is enhanced.[3] Knowledge of the changes in the polyamide matrix upon hydration would increase our understanding of the impact of water upon its mechanical behavior.

The role of water in polyamides has been the subject of intensive research employing a variety of techniques. Small-angle neutron scattering (SANS) work[4] on D_2O in nylon 6 and nuclear magnetic resonance (NMR) work[5,6] on wet deuterated nylon 66 have shown that water molecules penetrate into the amorphous phase but not into the crystalline phase of the polyamides. In dry nylon 66 the $-CH_2-$ groups undergo librational and internal rotational motions, but the presence of water in the amorphous regions causes a portion of the methylene groups to undergo isotropic molecular motion that is fast on the time scale of the line shapes ($\sim 10^5$ Hz). Such rapid motion is also observed for the methylene groups at temperatures above T_g. Furthermore, D_2O can undergo exchange with the amide hydrogen.[4] Chain motion in the crystalline regions of nylon 66 is unaffected by water. However, water does effect some structural changes in the crystals of nylon 6 by reversibly increasing the lamella spacing and decreasing the unit cell volume in the preexisting lamella.

Concerning the nature of water in polyamides, several authors[7,8] have postulated that water disrupts interchain hydrogen bonding between the NH and CO groups by forming new hydrogen bonds with them. Puffr et al. have proposed a mechanism of water absorption whereby three water molecules are hydrogen bonded to two neighboring amide groups. The first water molecule acts as a bridge between the two CO groups, viz. CO- - -HOH- - -OC, and is considered "strongly" bound water. Subsequent water molecules are "loosely" bound to the NH and CO groups. However, Le Huy et al.[9] proposed that all the water molecules are bound in the same way to the amide groups based on their study of glass transition (α) and secondary transition (β) in polyamides swollen by water, alcohol, and acid. The literature is also not clear as to what is the motional state and time scale of motion of water at the amide sites.

In this paper we present the results of a deuterium NMR study of various concentrations of D_2O in polyamide 6. Relaxation and solid echo experiments can provide valuable information about the types and correlation times of motions of the solvent molecule in an isotropic media as well as chemical exchange rates.[10,11] 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

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

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

where ω_0 is the Larmor frequency of the deuteron, $eeQq/h$ is the quadrupolar coupling constant of the OD bond, and J_0, J_1, and J_2 are the spectral densities. If the solvent molecules undergo isotropic reorientation with correlation time τ_c, the spectral densities take on the following forms:

$$J_0 = \tau_c \tag{3}$$

$$J_1 = \frac{\tau_c}{1 + \omega_0^2\tau_c^2} \tag{4}$$

$$J_2 = \frac{\tau_c}{1 + (2\omega_0)^2\tau_c^2} \tag{5}$$

T_1 time constants are determined by the inversion

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Table 1. Humidity Conditions

satd salt solution	% humidity	satd salt solution	% humidity
KNO_2	45	$NaClO_3$	75
$NaHSO_4$	52	KBr	84
$NaNO_2$	66	$NaBrO_3$	92

recovery experiment, which is also able to distinguish between components with different T_1 in the sample.

Experimental Section

Two millimeter diameter PA6 rods were purchased from Goodfellow Corp., and D_2O was obtained from Cambridge Isotope Laboratories. The molecular weight of the polyamide was found to be 60 000 g/mol from viscometry measurements. Differential scanning calorimetry (DSC) results showed that the crystallinity of the material is about 30%. Without any further modification the rods were dried in a vacuum at 100 °C for 48 h to remove trace water. The rods were then placed in containers of various humidity conditions for more than 1 month and allowed to equilibrate. Table 1 shows the saturated salt solutions used to prepare the different humidity environments at room temperature.[12] Equilibrium was considered attained when no weight change was recorded on successive days. To prepare polyamide 6 rods that were fully saturated with D_2O, the rods were simply immersed in liquid D_2O, henceforth represented by $(D_2O)_l$.

T_g measurements for the PA6 rods with different D_2O content were obtained by dynamic mechanical analysis on DMS-200 (Seiko Dynamic Mechanical Rheology Station). The loss tangent, tan δ, were measured in the range −50 to 100 °C at a heating rate of 5 °C/min. The frequency of the mechanical oscillation was 1 Hz.

The NMR work was done at room temperature (22 ± 1 °C) on a home-built probe and spectrometer operating at 45.8 MHz for deuterium. The 90° pulse time was 2.0 ± 0.1 μs. Free induction decays (FID) were obtained by using a single 90° pulse, and T_1 experiments were done by inversion recovery:[13] [180x−τ−90y−acquisition]. For both the rods placed directly in $(D_2O)_l$ and in the 92% humidity container, the digitization rate used was 10 μs with a total acquisition time of 10.24 ms. For the remaining samples the dwell time was 1 μs with total acquisition times between 512 and 1024 μs. Solid echo experiments were done using the pulse sequence [90x−τ−90y−τ−acquisition] with phase recycling and τ = 20 μs. The digitization rate was 1 μs, and the total acquisition time was 8192 μs.

Results and Discussion

Figure 1 shows the percentage weight gained by the PA6 rods at equilibrium plotted against humidity. The weight gained by the rods increases with increasing humidity. The rods that were soaked in D_2O gained 12% in weight. Figure 2 shows the spectra of the PA6 rod fully saturated with D_2O obtained from the solid echo experiment. The narrow Lorentzian line shape is due to D_2O, and it is superposed on a broader Pake powder pattern. The broad component of the spectra is the result of ND, which is formed from the exchange of NH groups in the amorphous regions with D_2O.[4] It is similar to the spectrum obtained when the rod was heated and dried in a vacuum to remove D_2O. The presence of both components in the line shape implies that the rate of exchange of between ND and D_2O is slow compared to the frequency separation between the ND signal and the D_2O signal, indicating the exchange time constant is slower than 10^{-5} s. (See Table 2 for characteristic times of the various processes.) A similar

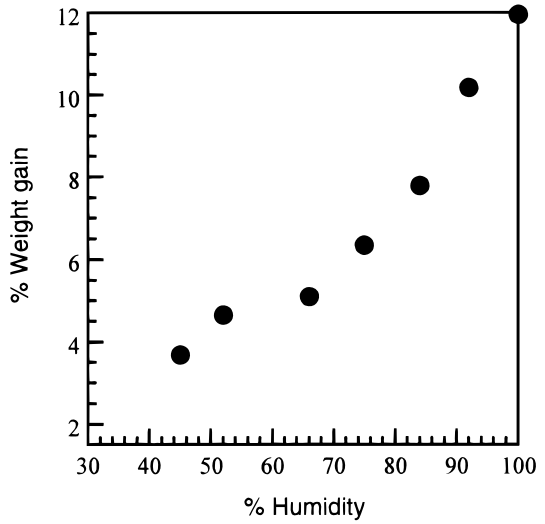

Figure 1. Percentage weight gained by PA6 rods at equilibrium vs percent humidity.

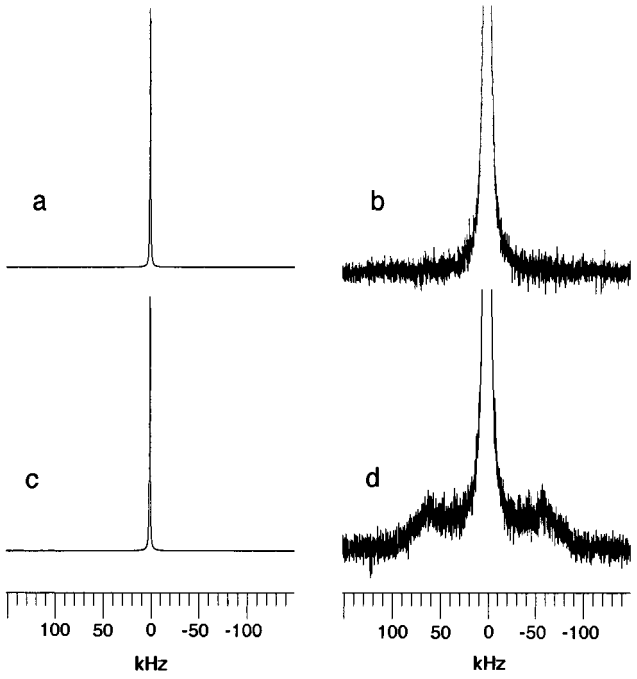

Figure 2. Deuterium NMR spectra of PA6 rod fully saturated with D_2O: (a) using one pulse sequence with dwell time of 10 μs; (b) spectrum a magnified 116×; (c) using solid echo sequence with dwell time of 1 μs; (d) spectrum c magnified 116× showing both the narrow line arising from the absorbed D_2O and broad Pake pattern of the ND groups resulting from isotopic exchange.

Table 2. Characteristic Times (in s) of Various Processes[a]

NMR		D_2O in PA6	
$1/\omega_0$	2×10^{-8}	τ_R	$<5 \times 10^{-9}$
T_2* (FID)	10^{-4}	τ_T	$<6 \times 10^{-4}$
		$\tau_{exchange}$	$>10^{-5}$

[a] Note: $\omega_0\tau_R \ll 1$, fast motion limit; narrow lines; $\omega_0\tau_T \gg 1$, slow motion limit.

phenomenon is observed for water molecules in epoxy resin systems.[14] Thus, there are two distinct deuterium environments—absorbed D_2O and ND—that can be resolved in the short dwell time FID. However, in the longer dwell time FID, the broad component is not detected. Thus, only the narrow line is observed. The

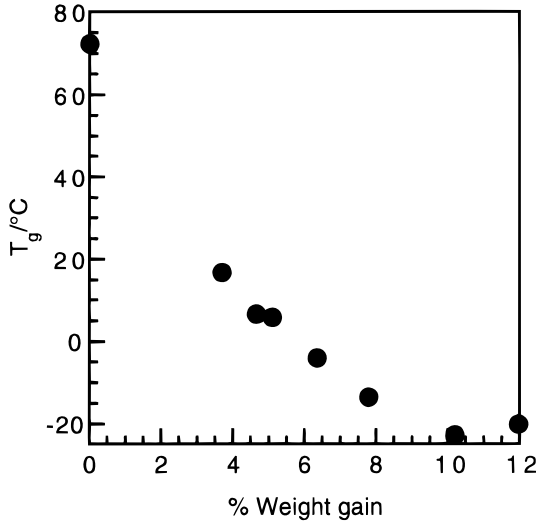

Figure 3. T_g/°C of PA6 rods vs percentage weight gained by PA6 rods at equilibrium.

remaining spectra reported in this work will show only the narrow component corresponding to absorbed D_2O.

T_g of the polyamides at various degrees of saturation are plotted in Figure 3. The T_g of the dry material is 72 °C and decreases with increasing amount of moisture as the polymer matrix becomes more plasticized. Figure 4 shows how the room-temperature deuterium NMR line shapes vary with D_2O content of the PA6 rods. All spectra show a single narrow Lorentzian line, indicating isotropic reorientation with a correlation time that is fast relative to the quadrupolar interaction (~200 kHz). The narrowest line is for $(D_2O)_l$, indicating, as expected, that D_2O reorients more rapidly in the pure liquid than in the polyamide. The next narrowest line is observed for the PA6 rod fully saturated with D_2O, and the line width broadens as the amount of D_2O in the polymer decreases. Thus, the correlation time of motion of D_2O increases in the less hydrated rods due to more restricted mobility as indicated by the higher T_g. We did not observe any sharp central peaks of line width less than 50 Hz which would have indicated the presence of free isotropic water in the polymer samples.

Figure 5 shows the spectrum of a rod that was fully saturated with D_2O and had undergone homogeneous uniaxial tensile deformation to a finite strain. A splitting—which may be due to anisotropic motions[15] or isotropic processes in anisotropically distributed sites or both (work is under way to investigate this phenomenon)—is observed which is characteristic of probe molecules in oriented polymers.[16,17] This splitting reduces overlap in the center of the spectrum, making it easier to determine whether a narrow central peak is present. Again we did not observe any narrow central peak arising from free water. This result directly contradicts the work of Hutchison and co-workers[16] where a large central peak was seen. This discrepancy may arise from differences in intrinsic morphological differences due to processing history as well as sample geometry. In this work, a single PA6 rod was employed, and the surface of the rod was wiped to remove excess liquid from the surface prior to NMR examination. In the Hutchison work, multiple fibers were bundled together to create an NMR sample. In such a configuration, it is more difficult to remove excess liquid trapped between fibers. Such trapped liquid would give rise to a narrow central peak even after deformation.

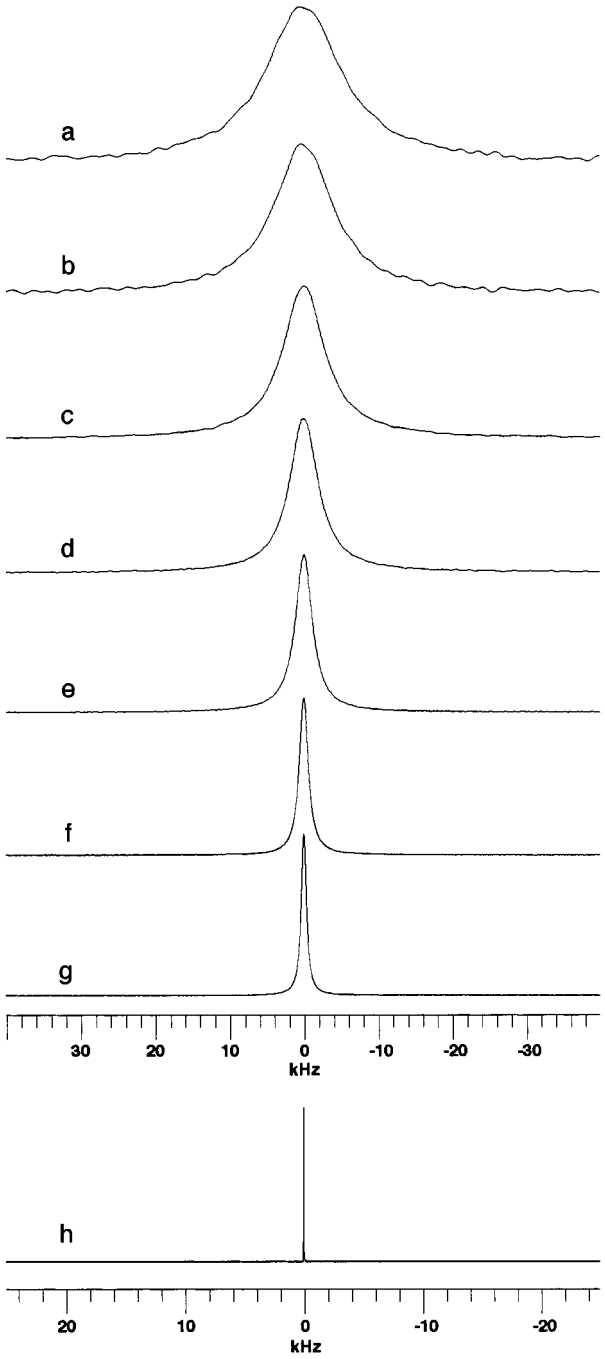

Figure 4. Deuterium NMR spectra of (h) $(D_2O)_l$ and (a)–(g) varying amounts of D_2O in PA6 rods at equilibrium. The percentage weight gained by PA6 rods is (a) 3.7, (b) 4.6, (c) 5.1, (d) 6.4, (e) 7.8, (f) 10.2, and (g) 12.0.

Data from inversion recovery experiments were well described by a single-exponential decay. Figure 6 shows the plot of T_1 versus percentage weight gain in the polyamide rods. The graph exhibits a minimum that puts the time scale of motion on the order of $\omega_0\tau_c \sim 1$. The T_1 minimum at 6.4% weight gain corresponds to $\tau_c = 1/\omega_0 = 1.28$ ns. A T_1 minimum has also been observed for the proton T_1 versus water content in silica gel.[18] The T_1 of $(D_2O)_l$ was measured to be 340 ms.

For the PA6 rods, T_2^* is obtained from the line widths of the spectra using the following equation:

$$1/T_2^* = \pi(\text{line width}) \qquad (6)$$

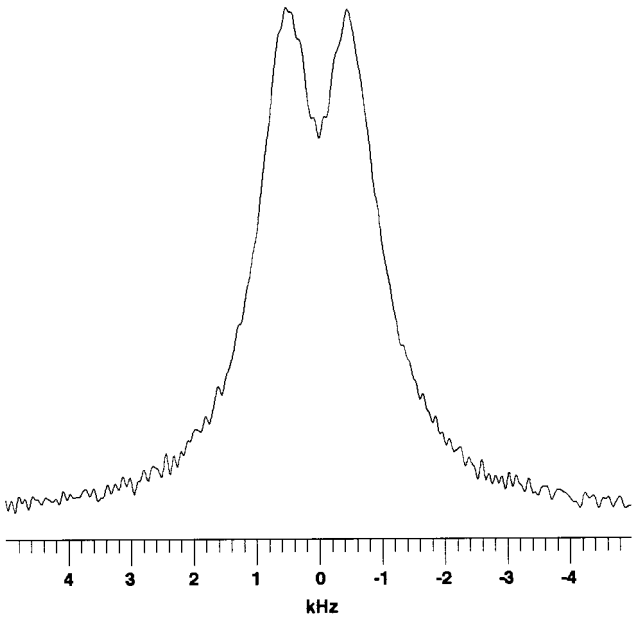

Figure 5. Deuterium NMR spectrum of D_2O in a stretched PA6 rod.

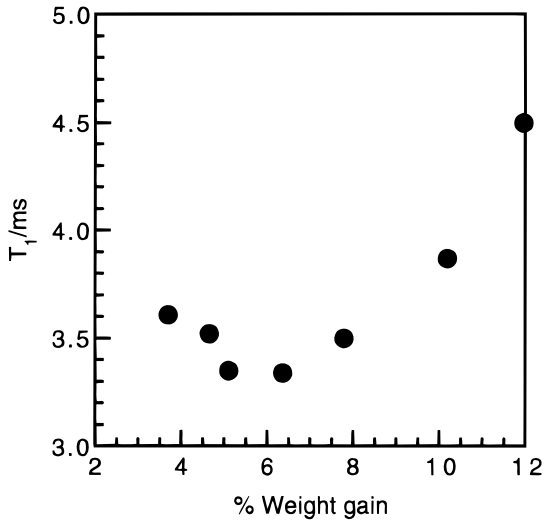

Figure 6. T_1/ms of D_2O in PA6 rods vs percentage weight gained by PA6 rods at equilibrium. The T_1 minimum at 6.4% weight gain corresponds to $\tau_c = 1/\omega_0 = 1.28$ ns.

Due to the short T_1 and T_2 time constant of the samples, spin-echo experiments could not be used to measure T_2 directly. The value of T_2* was assumed to equal to T_2 as field inhomogeneity effects are small (less than 50 Hz) compared to the line widths of D_2O in PA6. Figure 7 shows T_2 increasing monotonically with D_2O content.

Initially, the correlation times of motion of D_2O were calculated from T_1 and T_2 data using eqs 1−5 where we assume isotropic reorientation and a single correlation time for the spectral densities. The quadrupolar splitting for OD bond was taken to be 213.2 kHz.[19] However, this resulted in the τ_c obtained from eq 1 using T_1 data to be 2 orders of magnitude larger than those calculated from eq 2 using T_2 data. From eqs 2−5, at $\omega_0\tau_c = 1$, the theoretical value of T_2 is calculated to be 1.45 ms, corresponding to a line width of 220 Hz which is much less than those observed in the spectra. Since T_2 is sensitive to slow motions due to the J_0 term, the discrepancy between the correlation times was attributed to a slow-motion process experienced by the

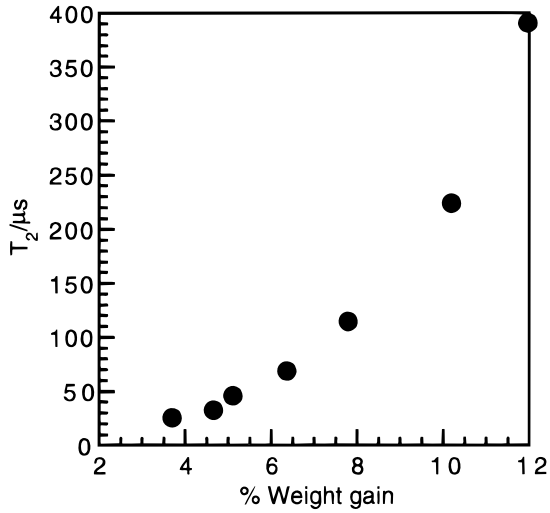

Figure 7. T_2/μs of D_2O in PA6 rods vs percentage weight gained by PA6 rods at equilibrium.

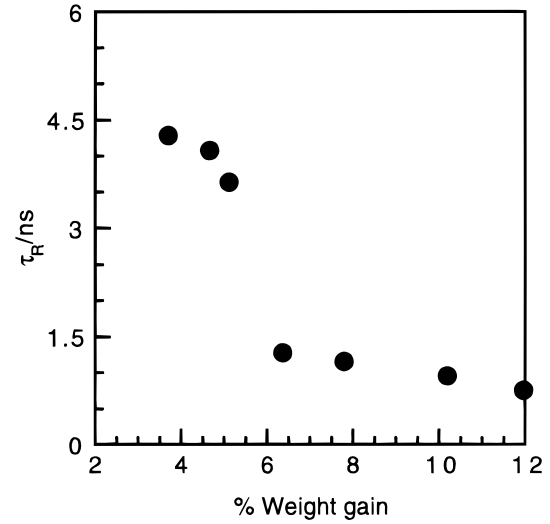

Figure 8. Rotational correlation time τ_R of D_2O in PA6 rods vs percentage weight gained by PA6 rods at equilibrium.

D_2O molecules. Freed[20] has treated in detail numerous factors that affect nuclear relaxation of small solutes in thermotropic liquid crystals. This theory was applied by Vold et al.[21] to model the behavior of small molecules in thermotropic nematic liquid crystals. Some of the factors considered are solute reorientation, coherent fluctuations in the nematic medium, and slow processes such as translational diffusion.

We adopt a simplified version of Freed's model by incorporating an additional correlation time due to translational diffusion to the J_0 term[21] in order to account for the slow process, such that

$$J_0 = 2\tau_R + 4\epsilon^2\tau_T \qquad (7)$$

where $\tau_R = \tau_c$ and τ_T are the rotational and translational correlation times, respectively. ϵ^2 is the mean-square fractional change in the quadrupolar coupling and is assumed to be 1%.[21] The resulting graphs of τ_R and τ_T versus percentage weight gained by PA6 rods are shown in Figures 8 and 9, respectively. The rotational correlation times are on the order of nanoseconds whereas the translational correlation times are in the millisecond range. The increase of both correlation times with decreasing amount of D_2O in the rod is to be expected

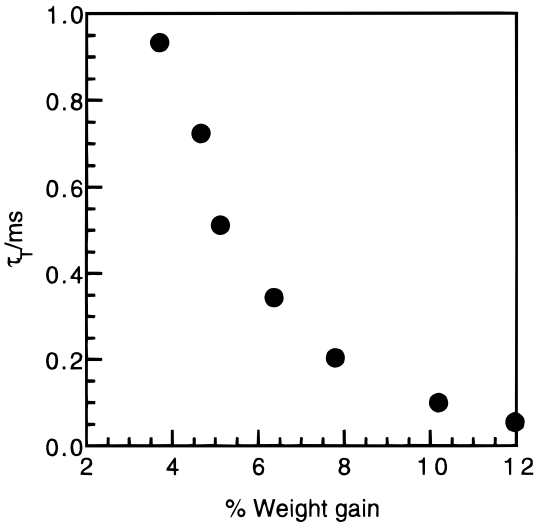

Figure 9. Translational correlation time τ_T of D_2O in PA6 rods vs percentage weight gained by PA6 rods at equilibrium.

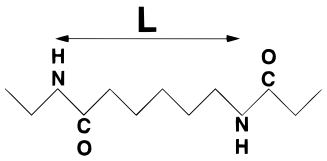

Figure 10. The α crystal structure of PA6 chain showing the distance $L = 8.70$ Å between consecutive NH groups.

since the mobility of the solvent molecules would be more restricted in the less plasticized polyamide matrix.

To obtain a better physical interpretation of τ_T, the diffusion coefficient, D, was calculated using the following equation:

$$D = L^2/\tau_T \tag{8}$$

where L is taken to be 8.70 Å, which is the distance between consecutive NH groups along a single polyamide 6 chain in the α crystal phase[22] (see Figure 10). In the amorphous phase we would expect L to be less than 8.70 Å due to the disordered nature of the chains. Hence, this value for L represents an upper limit in the amorphous region. The resulting values for the diffusion coefficient range from 8.10×10^{-12} cm^2/s for the lowest value of τ_T to 1.36×10^{-10} cm^2/s for the largest value of τ_T. Hernandez et al.[23] have also examined the diffusion of water in nylon 6 and found that the diffusion coefficient is fairly constant over the entire range of water volume fraction. They have obtained an average value of $D = 1.4 \times 10^{-10}$ cm^2/s, which falls within the same range that we have. Hence, the translational diffusion correlation time is consistent with D_2O molecules hopping from one amide site to another within the amorphous phase.

Our T_1 data show that there is only one relaxing component regardless of the water content. This implies that either the "tightly" and "loosely" bound water[7] have similar T_1 or there is only one type of water[9] in the polymer matrix. If a D_2O molecule is "tightly" bound between two CO groups as suggested by Puffr and coworkers, then we should expect it to undergo two-site flips about the bisector axis. Such a behavior was observed in rhyolitic glasses at room temperature[24] and resulted in the deuterium NMR spectrum showing a tentlike pattern. That such a spectrum was not observed for D_2O in polyamide 6, even at low D_2O content, suggests that the molecule is able to undergo isotropic reorientation at the amide site even though it is associated to the latter by hydrogen bonding. Hence, it is more likely that D_2O exists in one state in the polymer.

Conclusion

The motion of water in PA6 can be modeled as isotropic reorientation at the amide site where it is closely associated by hydrogen bonding and as translational diffusion between such sites. T_1 and T_2 measurements indicate that the correlation times for both types of motions decrease with increasing water content as the polymer matrix becomes more plasticized. Line shape analysis and T_1 data also indicate that there are no "free" water molecules. Furthermore, our results suggest that, for the range of water contents in the PA6 investigated, there seems to be only one state of water molecules in the polymer regardless of the amount of water. Finally, solid echo experiments show that there is slow exchange between deuterium oxide and the ND bonds of PA6 at a time scale of about 10^{-5} s.

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