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Segmental Dynamics in the Amorphous Phase of Nylon 66: Solid-State ^{2}H NMR[†]

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ABSTRACT: Solid-state deuterium NMR spectroscopy coupled with line shape simulations has been used to examine the segmental dynamics of individual methylene sites and N–D sites within the amorphous domains of selectively deuterated nylon 66 polymers over a wide temperature range. Magnetization only from amorphous domains may be isolated via spin–lattice relaxation time discrimination due to the presence of small-angle fluctuations (librations) at all sites within the amorphous domains above −50 °C. The N–D sites exhibit very little motion below T_g, and above T_g a fraction of the sites undergo nearly isotropic motion. The C–D sites exist in two discrete environments below T_g (*not a continuous distribution*): one of the populations exhibits only librational motion and the other exhibits both librational and internal rotation (γ-relaxation) motions. Above T_g, a fraction of the C–D sites undergo nearly isotropic motion (essentially the same fraction as the N–D sites), and this behavior of the entire repeat unit is identified with the α relaxation. The addition of 2 ± 0.3 wt % water has no apparent effect upon the γ relaxation and depresses the α process by approximately 40 °C; additionally, T_2 relaxation data indicate that the β relaxation is a process which involves all C–D sites and is observed only in wet polymer.

Introduction

In the previous paper in this issue,[1] the dynamics of each chemically distinct methylene group (C–D) and the N–D bond in the amide linkage located within crystalline domains of nylon 66 have been characterized over a wide temperature range with ^{2}H NMR methods. In the present paper, the analysis of data which is attributable to specific noncrystalline or amorphous domains is described. The molecular motions observed with these methods in various portions of the repeat unit located within crystalline domains are not associated with any of the previously observed mechanical or dielectric relax-

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ations; this is because the type of molecular motion observed in these domains is one in which the rate of motion does not change substantially with temperature, but the amplitude of motion changes significantly. In the noncrystalline domains, specific relaxation processes (α, β, γ) previously observed via dielectric and/or anelastic relaxation[2] can be directly identified with specific sites within the repeat unit, and for the α and γ relaxations the trajectory of molecular motion is established. Previous efforts[3] to characterize the types of segmental motion extant for either nylon 66 or nylon 6 with NMR methods have been unable to provide a unique interpretation of the data due to a lack of both molecular and morphological specificity.

The experimental methodology that has been used to generate ^{2}H NMR line shapes and associated relaxation data which are characteristic of polymer segments only in noncrystalline domains over the temperature range ~ -50 to 228 °C has been described previously.[1] In the temperature range ~ -100 to ~ -50 °C, spin-lattice discrimination is still effective, but a portion of the magnetization from noncrystalline domains is attenuated by T_2 relaxation. Below -100 °C, there is progressively more mixing of magnetization arising from noncrystalline domains with that arising from crystalline domains as the temperature is decreased; however, the vast majority of the relaxation and line shape changes which occur as a function of temperature are observed above ~ -100 °C, so this is not an impediment.

Experimental Section

^{2}H NMR spin-lattice relaxation time discrimination was used to distinguish between magnetization arising from crystalline and noncrystalline domains. Values of T_2 for the noncrystalline component were obtained by fitting the decay of the partially relaxed echo amplitude to an exponential form as a function of the pulse spacing (τ_1) in a radio-frequency quadrature pulse pair. These experimental methods and all other NMR experiments employed to generate the data in this paper, as well as details of the line shape and relaxation data analysis, are described in the previous paper.[1]

The preparation of selectively deuterated and ^{13}C-labeled dry nylon 66 polymers has been previously described.[1,6] Polymers containing a well-defined amount of water were prepared by the procedure given here. Small semicrystalline polymer particles (~0.5 mm) that had been previously melt equilibrated (to provide a most probable molecular weight distribution) and annealed at 238 °C for 20 min were boiled in water for about 150 h. Subsequent to this process, thermogravimetric analysis revealed that the samples contained ~8 g of water per 100 g of polymer and thus were fully saturated.[7] Polymers containing 2 ± 0.3 wt % water (as determined with control samples) were prepared by evacuating the fully saturated polymer under vacuum in an NMR tube at 60 °C for 3 h; subsequently, the sealed tubes were heated at 70 °C for 150 h to ensure uniform distribution of the water within the sample.

Results and Discussion for Dry Nylon

Partially and fully-relaxed ^{2}H NMR spectra and associated relaxation data were obtained with the use of quadrupole echo sequences.[1,8] Spin-lattice relaxation of the selectively deuterated methylene groups was strongly nonexponential and was easily decomposed in the time domain into two components whose relaxation times differed by at least a factor of 24 over the temperature range -150 to 230 °C. Data for the N-D-labeled polymer was similarly decomposed into two components at temperatures above -50 °C. The component of the magnetization with the smaller spin-lattice relaxation time may be associated with the noncrystalline domains.[1] Because the two spin-lattice relaxation times differ by such a large factor, magnetization can be selectively generated from the noncrystalline domain by using a delay (τ_0) in the saturation recovery sequence equal to 5 times the value of the smaller spin-lattice relaxation time.

The discussion portion of this paper is divided into sections for both dry and wet nylon and further subdivided into discussions of the dynamics of individual sites above and below T_g. The glass transition of dry nylon 66 is ~50 °C at low frequency, ~100 °C at the frequency relevant to the line shape analysis (~100 KHz), and ~150 °C at the frequency relevant to the spin-lattice relaxation time analysis (~100 MHz).[2] The temperature of the glass transition is not only a function of the frequency of the measurement but is also a strong function of the water content and is expected to be depressed by approximately 40 °C with 2 wt % water.[7]

N-D Motion below T_g. The ^{2}H NMR line shapes of the N-D-labeled polymer below ~100 °C are quite close to the rigid pattern found for the crystalline phase (η = 0.17 and ν_Q = 191 kHz) at similar temperatures and indicate that there is very little motional averaging taking place. Additionally, the absence of any T_2 distortion (as a function of τ_1 in the quadrupolar echo sequence) demonstrates that the very slight averaging of the line shape is due to a fast motion ($\nu_c > 10^7$ Hz). The minor amount of averaging observed for these line shapes is well fit by a model of rapid small-amplitude librations about the N-C axis as is present in the crystalline phase above the Brill transition.[1] The inhomogeneous distribution of librational amplitudes ($P(\Delta\theta)$) is conveniently described by a Gaussian distribution of standard deviation $\Delta(\Delta\theta)$ truncated at $\Delta\theta_0$ to produce a half-Gaussian distribution where $P(\Delta\theta) = 0$ for $\Delta\theta < \Delta\theta_0$. (A Gaussian distribution is used because it is the simplest, physically realistic distribution that will fit the data, and this type of distribution is commonly used to describe highly disordered systems; it must be cut off in the low-angle region due to zero-point vibrations, and the center of the distribution is the simplest choice.) Each libration within this distribution is described by a homogeneous Gaussian azimuthal distribution of standard deviation $\Delta\theta$. At 97 °C (see below), $\Delta\theta_0 = 6°$ and $\Delta(\Delta\theta) = 7°$, indicating that even at a temperature very close to T_g the motion of the N-D sites is very restricted. It is possible to estimate the time scale of these small-angle fluctuations by correlating the line shape analysis with the spin-lattice relaxation time.[1] This procedure produces a value for the correlation frequency $\nu_c = (2\pi\tau_c)^{-1}$ of 5×10^8 Hz. (The correlation time, τ_c (s/rad), is the time constant of the correlation function, which is assumed to be exponential.) These results indicate that the N-D bonds can be considered to be essentially static below T_g, and the type of motion (libration) is quite similar to the motion observed for the N-D bonds in the crystalline domains at all temperatures below 230 °C. Parenthetically, we note that equally good agreement with the experimental data can be found by using a multisite large-angle jump model where only one of the sites is appreciably populated (i.e., the restriction of the motion would be energetic rather than geometric); however, such a motion can be eliminated as a possible model for the "constrained" methylene segments on the basis of T_2 results (see below and the accompanying paper) and therefore seems unlikely to be a reasonable model for the motion of the N-D bonds.

C-D Motion below T_g. In contrast to the very limited amount of motional averaging observed for the N-D line shapes, the C-D line shapes are indicative of a very

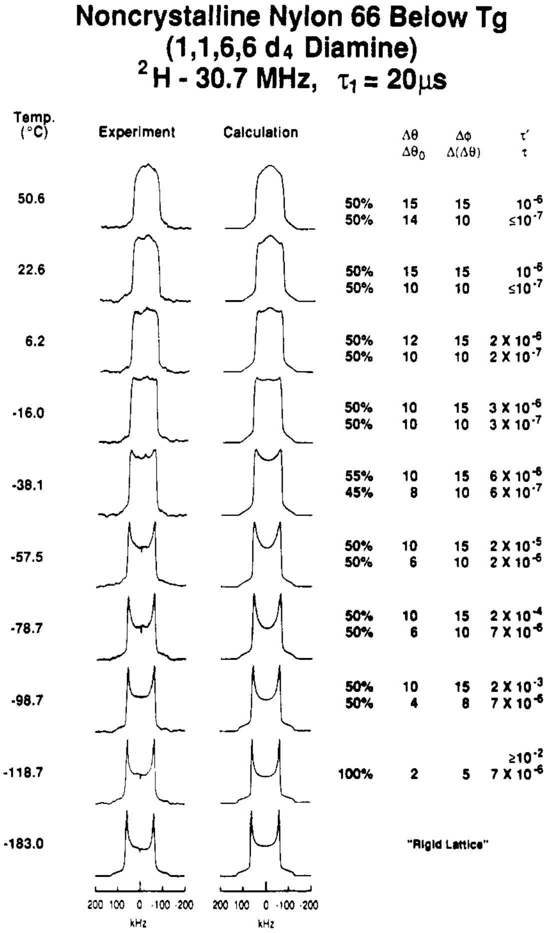

Figure 1. Experimental and calculated ^2H NMR line shapes, with $\tau_1 = 20$ μs, for the noncrystalline fraction of NY16NHME as a function of temperature below the glass transition temperature. The parameters used to calculate the line shapes are given in the right-hand side of the figure. The relative population of the mode II motion is given first followed by the standard deviation of the fast-exchange libration ($\Delta\theta$), the standard deviation of the inhomogeneous distribution of azimuthal jump angles centered at 120° ($\Delta\phi$), and the residence time of this latter motion (τ'). The next line gives the relative population of the mode I motion followed by the low-amplitude cutoff of the inhomogeneous Gaussian distribution of librational amplitudes ($\Delta\theta_0$), the standard deviation of the inhomogeneous Gaussian distribution of librational amplitudes $\Delta(\Delta\theta)$, and the characteristic librational lifetime (τ) (see text).

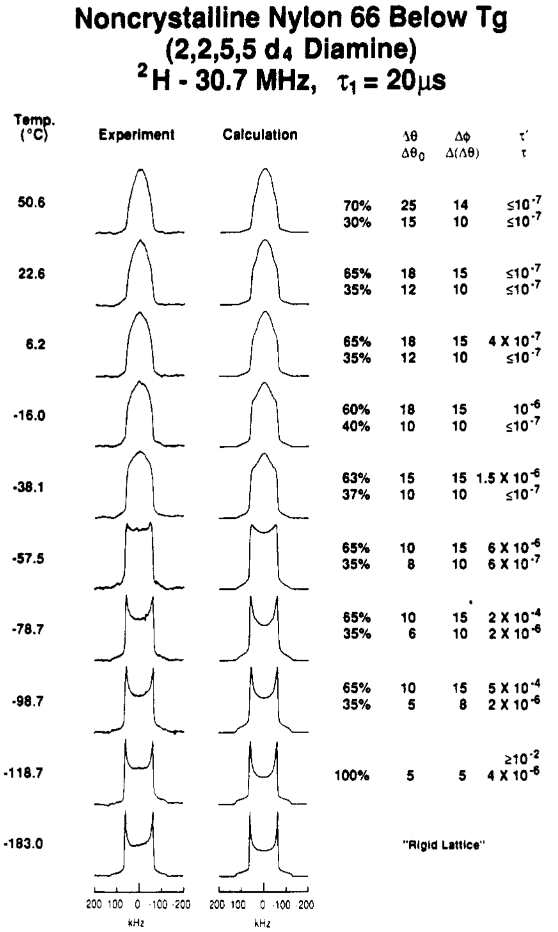

Figure 2. Experimental and calculated ^2H NMR line shapes, with $\tau_1 = 20$ μs, for the noncrystalline fraction of NY25NHME as a function of temperature below the glass transition temperature. The parameters used to calculate the line shapes are given in the right-hand side of the figure and are defined in the caption to Figure 1 and in the next.

substantial amount of motional averaging for a large fraction of each methylene site. Figures 1–5 illustrate the noncrystalline line shapes (the component of magnetization with the shortest spin–lattice relaxation time) for each of the nylon 66 polymers selectively deuterated at one of the chemically distinct methylene groups within the repeat segment for $\tau_1 = 20$ μs. (Polymers are identified by the site of selective deuteration: in the diamine moiety at the C_1 and the C_6 carbons (NY16NHME), in the diamine moiety at the C_2 and the C_5 carbons (NY25NHME), in the diamine moiety at the C_3 and the C_4 carbons (NY34NHME), in the adipoyl moiety at the C_3 and the C_4 carbons (NY34COME), and in the adipoyl moiety at the C_2 and the C_5 carbons (NY25COME) with some scrambling (~30%) to the N–D site.) From these figures, it is obvious that the line shapes depart from the "rigid lattice" Pake doublet pattern above -70 °C for all of the methylene groups, such that near room temperature the line shapes have a maximum intensity at zero frequency (rotating frame). Note that less motional averaging is observed for the methylene groups α to the amide linkage (NY16NHME and NY25CO).

Figures 6–9 show that the line shapes are quite strongly dependent upon the value of τ_1 even at temperatures below -70 °C, where the line shapes appear to be Pake-like for $\tau_1 = 20$ μs. The τ_1 dependence of these line shapes is due to anisotropic T_2 relaxation. The line shape distortions shown in Figures 6–9 are diagnostic[1] of small-angle fluctuations (jump like or diffusive). The features in the line shape that persist at larger values of τ_1 are associated with those orientations (or sites, see below) which are in the fast-exchange limit. Note that for NY25NHME and NY34NHME the T_2 distortion observed at lower temperatures is no longer apparent at room temperature. This latter result suggests that the decay of the solid echo amplitude as a function of τ_1 is entirely due to static dipolar interactions (both ^2H–^1H and ^2H–^2H); hence, the molecular motion must be fast ($\nu_c > 10^7$ Hz). In this limit, the line shape for these two polymers can be analyzed as a distribution of fast-exchange powder patterns, each of which is defined by an averaged asymmetry parameter (η^*) and coupling constant (ν_Q^*). These line shapes are well fit by the sum of two inhomogeneous distributions ($\eta^* \simeq 0$, $\nu_Q^* \simeq \nu_Q$ and $\eta^* \simeq 1$, $\nu_Q^* \simeq \nu_Q/2$) which are associated with "constrained" and "free" components[9] of the amorphous polymer, respectively.

Additional support for the use of a bimodal model of motion is available from the spin–lattice relaxation time measurements.[1] The spin–lattice relaxation time of the faster relaxing component of magnetization for all of the methylene groups is near 10 ms at room temperature and reaches a minimum near 0 °C. In the constrained por-

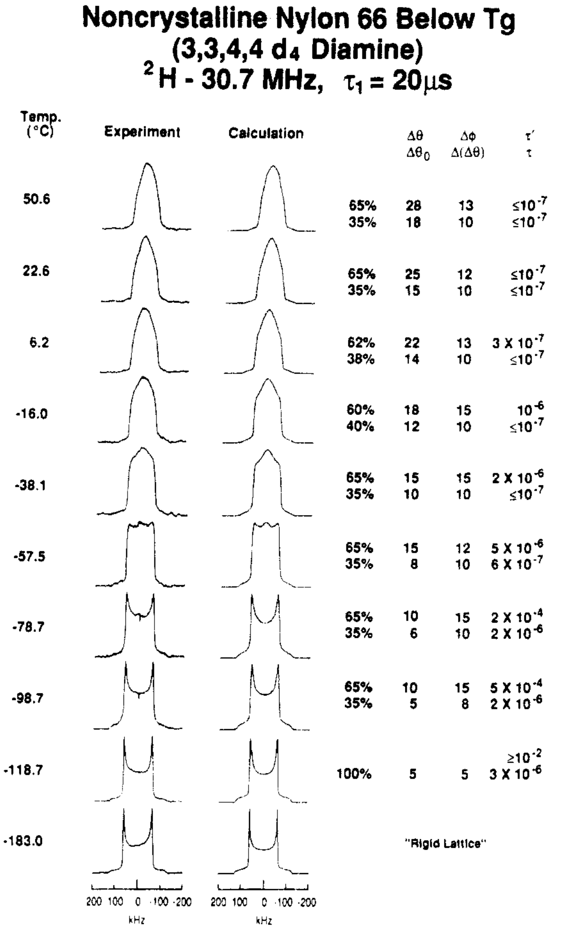

Figure 3. Experimental and calculated ^{2}H NMR line shapes, with τ_1 = 20 μs, for the noncrystalline fraction of NY34NHME as a function of temperature below the glass transition temperature. The parameters used to calculate the line shapes are given in the right-hand side of the figure and are defined in the caption to Figure 1 and in the text.

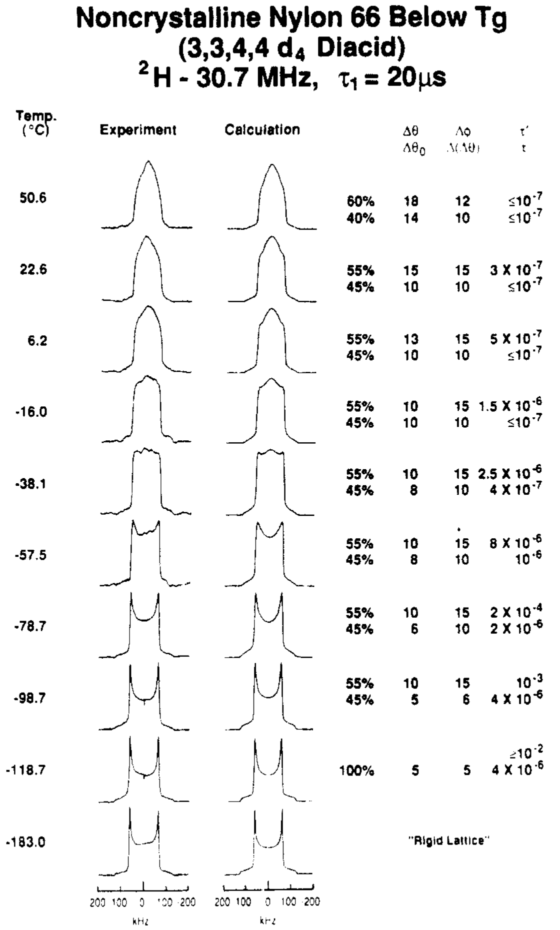

Figure 4. Experimental and calculated ^{2}H NMR line shapes, with τ_1 = 20 μs, for the noncrystalline fraction of NY34COME as a function of temperature below the glass transition temperature. The parameters used to calculate the line shapes are given in the right-hand side of the figure and are defined in the caption to Figure 1 and in the text.

tion, if the motion can be described by an inhomogeneous distribution of librations about one C–C bond, the room temperature relaxation time would imply that $\nu_c \simeq 2 \times 10^8$ Hz, which is quite close to the Larmor frequency of 3×10^7 Hz. For the free portion to also have a short spin–lattice relaxation time, it must also have a component of motion of a similar nature. In addition to this librational motion (called mode I), the free portion must have an additional motion (called mode II) to account for the additional motional averaging observed in the line shapes. A bimodal model is required to satisfy the observations that all of the magnetization associated with the noncrystalline domains appears, at these temperatures, as the short spin–lattice relaxation time component and that the line shapes reflect that there are at least two different populations with very different degrees of motional averaging. However, it is known that the bimodal character of an amorphous line shape can be modeled as a very large inhomogeneous distribution of correlation times (mode II),[10] where the intermediate-exchange line shapes are effectively unobservable due to a minimal population and rapid T_2 relaxation.[11] With this kind of model, the constrained and free portions would be associated with populations in the slow- and fast-exchange limits of mode II, respectively. This model will not fit all of the experimental data because the strong T_2 relaxation effects observed below room temperature (Figures 6–9) would require that the width of the distribution of correlation times increase substantially with increasing temperature (producing temperature-dependent slow- and fast-exchange populations), and the line-shape fits (Figures 1–5) require that the relative populations (fast and slow exchange in this model) be essentially independent of temperature. Therefore, we propose that a bimodal model is the simplest model consistent with the experimental data, with librational motion (mode I) operative in both free and constrained domains and that the mode II motion is operative only in the free domains. Additionally, in a semicrystalline polymer as opposed to a completely amorphous polymer, it is quite reasonable to postulate the existence of two subpopulations within the amorphous domains due to either morphological (e.g., chain folds/interfacial and free amorphous)[12] or local (hydrogen bonding) constraints.

The motion previously described as mode II is postulated to be an inhomogeneous distribution of trans–gauche jumps of the type usually ascribed to methylene segments, and the applicability of such a model is tested here by comparison with all of the experimental data. A trans–gauche isomerization model is suggested by the observation that the high-temperature line shapes of the free amorphous population approximate a fast-exchange two-site tetrahedral jump with $P_1 = P_2$ ($\eta^* = 1$, $\nu_Q^* = \nu_Q/2$). (Actually, ν_Q^* is slightly smaller than $\nu_Q/2$, but this is accounted for by a small amplitude libration of $\Delta\theta < 30°$.) If the dynamics are restricted to rotations about one C–C bond ($\beta = 109.5°$), a sequential model of motion[13] can be used to fit both components of the line shapes. A fast homogeneous libration of characteristic time τ (defined in the previous paper), with its spatial

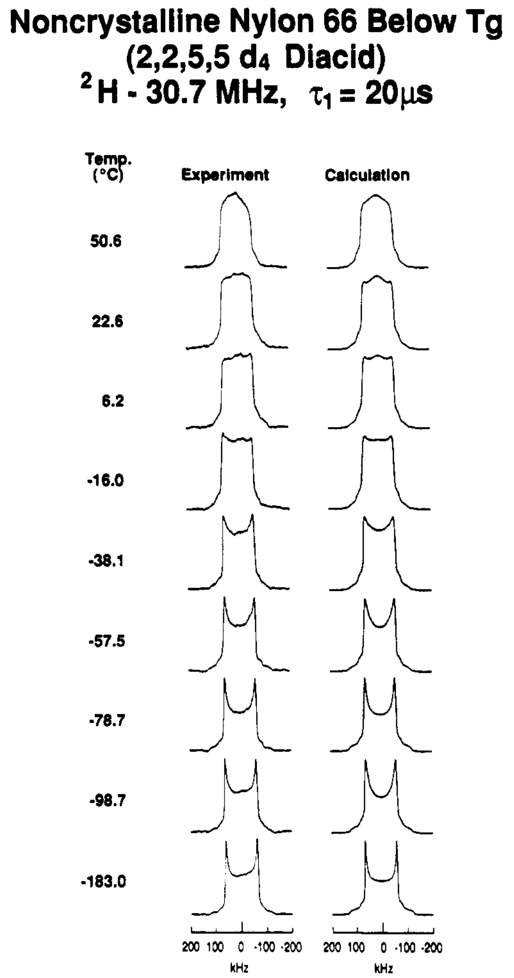

Figure 5. Experimental and calculated ^2H NMR line shapes, with τ_1 = 20 μs, for the noncrystalline fraction of NY25COME as a function of temperature below the glass transition temperature. Calculated line shapes are constructed from the simulations of NY16NHME (80%) (Figure 1) and the simulations of the rigid N-D polymer (20%).

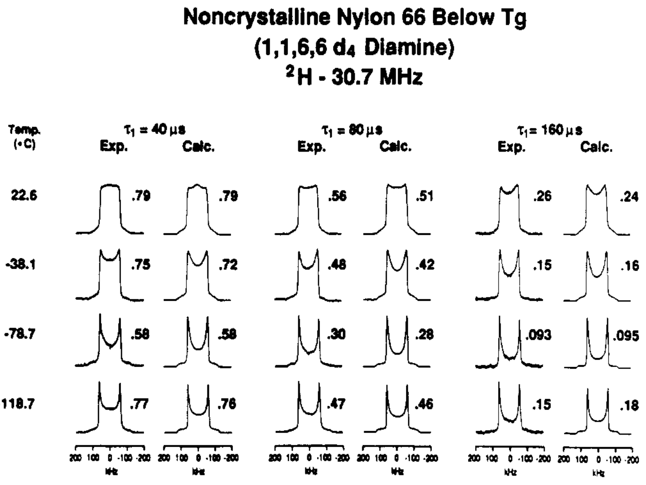

Figure 6. Experimental and calculated ^2H NMR line shapes, with τ_1 = 40, 80, and 160 μs, for the noncrystalline fraction of NY16NHME at selected temperatures below the glass transition temperature where T_{2d} is 200 μs at the three lowest temperatures and 230 μs at room temperature. The number adjacent to each line shape is the echo intensity normalized to the τ_1 = 20 μs intensity.

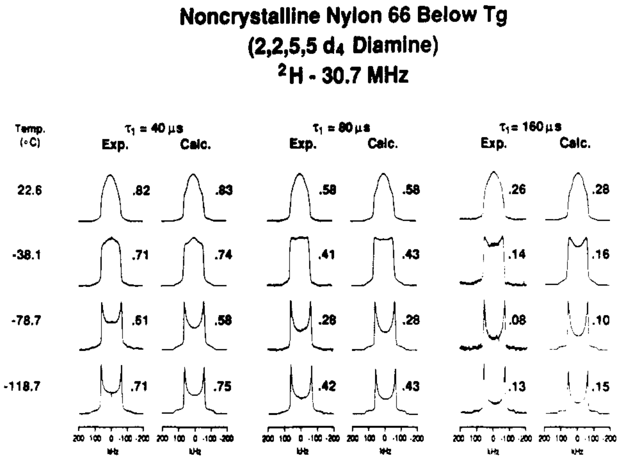

Figure 7. Experimental and calculated ^2H NMR line shapes, with τ_1 = 40, 80, and 160 μs, for the noncrystalline fraction of NY25NHME at selected temperatures below the glass transition temperature where T_{2d} is 190 μs at the three lowest temperatures and 220 μs at room temperature. The number adjacent to each line shape is the echo intensity normalized to the τ_1 = 20 μs intensity.

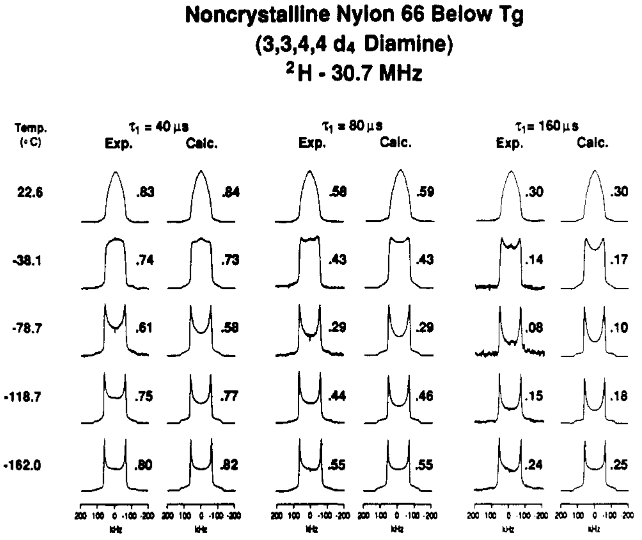

Figure 8. Experimental and calculated ^2H NMR line shapes, with τ_1 = 40, 80, and 160 μs, for the noncrystalline fraction of NY34NHME at selected temperatures below the glass transition temperature where T_{2d} is 200 μs at the three lowest temperatures and 230 μs at room temperature. The number adjacent to each line shape is the echo intensity normalized to the τ_1 = 20 μs intensity.

characteristic defined by $P(\Delta\theta)$, $\Delta\theta_0$, and $\Delta(\Delta\theta)$, is coupled with an inhomogeneous Gaussian distribution of azimuthal jump angles, of residence time τ', centered at the tetrahedral jump angle with standard deviation $\Delta\phi$. (It is the narrow inhomogeneous distributions of both librational and jumping amplitudes which smear out the distinctive singularities in the line shapes.) In practice, the line shapes of the free domains are calculated with a single fast-exchange Gaussian libration (to minimize the calculation time), and the line shapes of the constrained domain are modeled without any trans-gauche jumps (corresponding to $\tau' > 10^{-2}$ s/cycle). Additionally, the echo decay as a function of τ_1 due to static dipolar interactions is considered to be exponential with a relaxation time T_{2d} for both domains. The values of T_{2d} vary little with temperature (Figures 6–9), and the slight increase near room temperature is consistent with the spatial averaging observed in the line shapes (Figures 1–5). This model gives quite satisfactory fits of the amorphous line shapes and their τ_1 dependence at temperatures where $\tau \leq 10^{-7}$ s/cycle. At lower temperatures, the τ_1 dependence of the line shapes indicates that the librational motion in the constrained domains is no longer in the fast motion limit, and at these temperatures the libra-

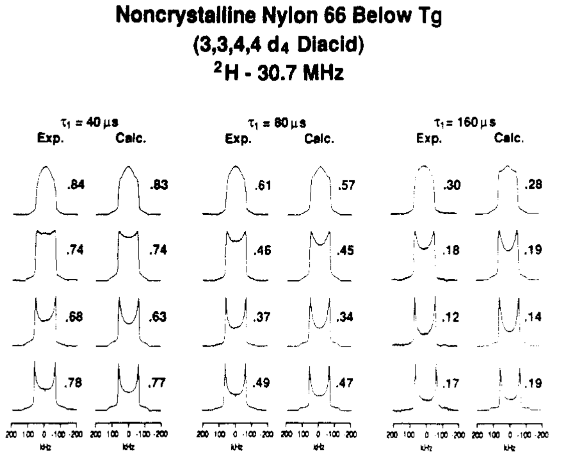

Figure 9. Experimental and calculated ^{2}H NMR line shapes, with τ_1 = 40, 80, and 160 μs, for the noncrystalline fraction of NY34COME at selected temperatures below the glass transition temperature where T_{2d} is 220 μs at the three lowest temperatures and 250 μs at room temperature. The number adjacent to each line shape is the echo intensity normalized to the τ_1 = 20 μs intensity.

tional motion is modeled as a small-angle fluctuation with $\tau > 10^{-7}$ s/cycle (see Figures 1–5). Furthermore, at very low temperatures (−120 °C) when the rate of the tetrahedral jump becomes so slow that the line shapes are insensitive to it, the entire line shape is fit with this small-angle fluctuation model.[14]

This model depends upon seven parameters: the fraction of constrained and free domains, the librational parameters ($\Delta\theta$, $\Delta\theta_0$, $\Delta(\Delta\theta)$, τ), and the internal rotation jump parameters ($\Delta\phi$, τ'). From the fits of the line shapes, Figures 1–5, it is apparent that the three parameters which reflect the spatial inhomogeneity of the system (the fraction of constrained and free domains, $\Delta(\Delta\theta)$, and $\Delta\phi$) are essentially independent of temperature for each site. This observation reaffirms the physical reality of our bimodal population model (some segments can not execute tetrahedral jumps) and is not consistent with a large distribution of correlation times model. The free domain population is somewhat larger for the NY25NHME and NY34NHME positions (65%) and the NY34COME position (55%) than for the NY16NHME and NY25COME (50%) positions, and these sites also exhibit a larger amplitude of libration ($\Delta\theta$). (This population difference indicates that the motion involves only two to four methylene groups and is not a large-scale segmental reorientation.) The larger fraction of free domain population and the larger amplitude of librational motion for the two interior methylene groups in the HMDA moiety, and to some extent for the interior methylene groups in the adipoyl moiety, indicate that methylene positions further away from the amide "pinning points" are able to execute a wider variety of types of motion than are those methylenes which are α to the amide linkage. The observation of inhomogeneous distributions of both large- and small-angle motions is not unreasonable in a polymeric glass, especially in a semicrystalline polymer.

The variation of the residence time of the jump motion (τ') in the free domains is illustrated in Figure 10. The temperature dependence of the jump rate ($1/\tau'$) for all of the methylene positions is in good agreement with the dielectric and mechanical relaxation data[2] for the γ relaxation and is found to have an activation energy of 8 kcal/mol. This value of the activation energy is in good agreement with previously reported data.[2] Note that a trans–gauche isomerization, unlike the π-flip of a phenylene group,[15] is expected to be mechanically active, but dielectric activity of such an isolated motion is questionable. It is possible that a small fraction of the amide groups (~1%) may be coupled to the methylene motion and could thus be responsible for the dielectric activity.[16] No evidence has been found in this study of dry nylon as to the origin of the rather weak β relaxation.[2]

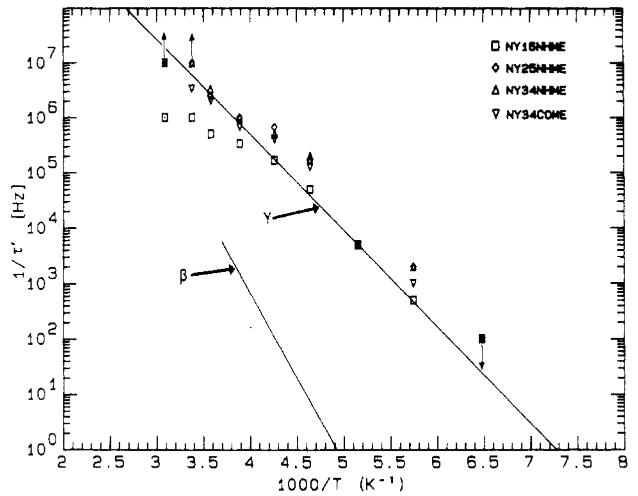

Figure 10. Calculated frequencies ($1/\tau'$) of near tetrahedral jumps as a function of inverse temperature for each methylene position (data points) in the noncrystalline domains. The solid lines are the dielectric and mechanical data for the β and γ relaxations.[2] The arrows at the highest (lowest) temperatures indicate where the data are no longer sensitive to the rate of the motion and the frequency could be larger (smaller) than indicated.

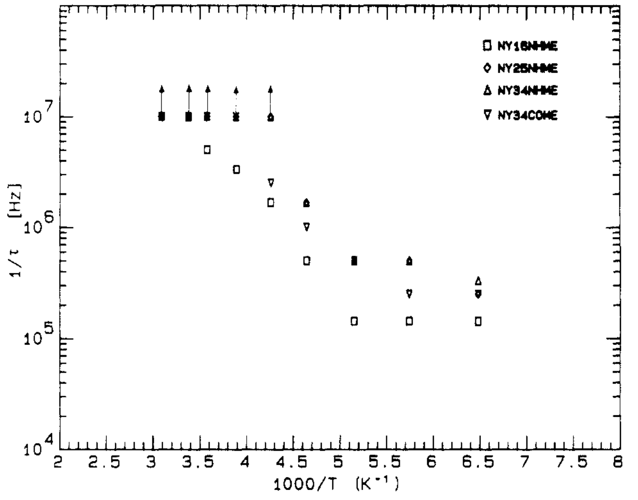

Figure 11. Calculated librational frequency of the mode I motion as a function of inverse temperature for each methylene position in the noncrystalline domains. The arrows at the highest temperatures indicate where the data are no longer sensitive to the rate of the motion and the frequency could be larger than indicated.

The temperature dependence of the rate ($1/\tau$) of the librational motion in the constrained domains is illustrated in Figure 11. The rate of this motion is found to always remain relatively close to the Larmor frequency (30.7 MHz) and has an activation energy of 4 kcal/mol, which is half of that observed for the internal rotation jump. The rate of this motion is much too slow to be a simple vibration and may reflect the time scale of the fluctuation of the local environment. As seen above (T_2 distortions), this motion is a small-angle fluctuation (small-angle jump or diffusive). Restricted and not necessarily fast diffusive motions have been previously proposed to model π-flips of the phenyl groups in polycarbonate.[17] Another indication of the existence of fast small-angle

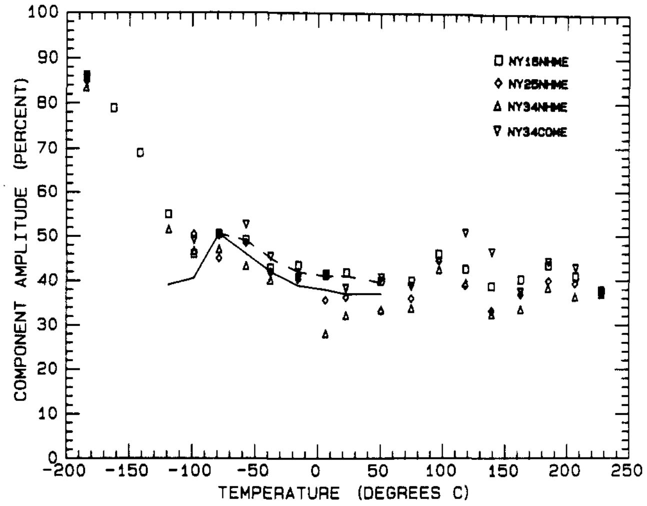

Figure 12. Relative amplitudes of the component of magnetization with the longest spin–lattice relaxation time as a function of temperature are shown as the individual data points for each methylene site. The correction to the amplitude for T_2 relaxation effects is shown as a dashed line for NY16NHME and as a solid line for NY25NHME, NY34NHME, and NY34COME.

fluctuations in the *entire* noncrystalline domain is given by the spin–lattice relaxation data. The relatively short value of the spin–lattice relaxation time of the portion with the shorter T_1 at -120 °C ($\simeq$0.4 s) is not consistent with any type of motion near the slow motion limit. Alternatively, the distribution of $P(\Delta\theta)$ available from the line shape fits allows us to estimate from the value of T_1 that 5×10^5 Hz $< 1/\tau < 10^6$ Hz. This range fits rather well with the values deduced from the line-shape analysis for mode I motion, 1.5×10^5 Hz $< 1/\tau < 3 \times 10^5$ Hz. Moreover, this result confirms that similar small-angle fluctuations (mode I) must occur in both the free and constrained domains and that the line shapes of the free domain are essentially insensitive to this motion when a near tetrahedral jump of comparable frequency is taking place. At low temperatures, the amorphous spin–lattice relaxation (thus the T_1 discrimination experiment) is controlled by the librational motion, which is very sensitive to the librational amplitude.[18] Hence, the smooth variation with temperature of the relaxation time of the shorter T_1 component is completely explained by the presence of the librational motion in the entire amorphous phase without invoking any model of a large distribution of correlation times.

The physically realistic model of motion described above is in quantitative agreement with the line-shape data (Figures 1–5), the T_2 anisotropy (Figures 6–9), and the T_1 data.[1] In particular, the component amplitudes in the spin–lattice relaxation data can be corrected for T_2 relaxation effects, and Figure 12 illustrates this correction. These results demonstrate that the fraction of magnetization with the longest spin–lattice relaxation time is still very close to 40% (above -50 °C) and is comparable to the percent crystallinity measured by DSC (40%) and X-ray (35%). Between -50 and -100 °C, most of the apparent increase of the fraction of the polymer with the longer spin–lattice relaxation time is due to T_2 relaxation in the amorphous domains, indicating that the T_1 discrimination is still effective; however, below -100 °C the large increase of this component with decreasing temperature reflects the fact that only a fraction of the material in the amorphous domains has the type of librational motion (mode I) necessary to give a short spin–lattice relaxation time. Furthermore, modeling mode I motion as small-angle fluctuations (diffusive or jump) has been shown to be correct. The model of mode II motion as a trans–gauche isomerization is consistent with all of the data, but there are other models of motion[1,19] which might give equally good agreement. (The trans–gauche isomerization model is favored here over models of large-amplitude restricted diffusion because only a discrete state model will appear as a thermally activated process (e.g., γ relaxation).) However, because the T_2 relaxation effects are mainly dependent upon the time scale of the motion, the time scale of the mode II motion and the relative fraction of constrained and free domains can be accurately determined regardless of the geometrical model. Note, finally, that a number of proposed models of segmental motion such as crankshaft, flip-flop, and counterrotation of second neighbor bonds are consistent with the mode II motion.

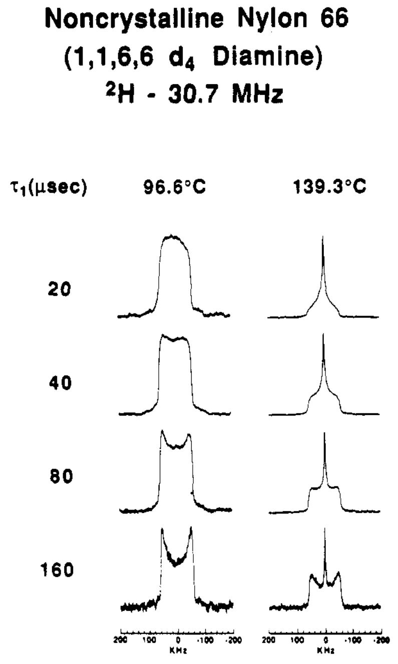

Figure 13. The τ_1 *dependence of the* ^{2}H NMR *line shape of* the noncrystalline component of NY16NHME at 96 and 139 °C.

N–D and C–D Motion above T_g. At temperatures above 60 °C, T_2 strongly decreases, and large T_2 distortions are observed at 96 °C for the C–D line shapes of NYNH16ME (Figure 13) and for the N–D line shapes at 139.3 °C (Figure 14). This demonstrates the presence of a new mode of motion which is still too slow to produce motional averaging of the line shapes but clearly affects the T_2 relaxation. At 118 °C and higher, a narrow component appears in the line shapes for all of the labeled samples (Figures 15–19) and is attributable to rapid ($\nu_c \gg 10^5$ Hz) nearly isotropic motion. The fraction of the line shape represented by this narrow component increases with increasing temperature and represents more than 80% of the line shapes above 200 °C. Clearly, the onset of this large-amplitude motion must be due to the α-relaxation or glass transition.[2] Unfortunately, for such a quasi-isotropic motion, the intermediate-exchange-rate line shapes are strongly attenuated due to strong T_2 relaxation.[20] A quantitative analysis of the data is very difficult, if not impossible, in this situation because the T_2 decay is nonexponential.[21] It appears that the experimental line shapes (Figures 13–18) may be represented as a composite of three components: segments undergoing fast, intermediate, and slow exchange. This representation, consistent with a broad inhomogeneous distri-

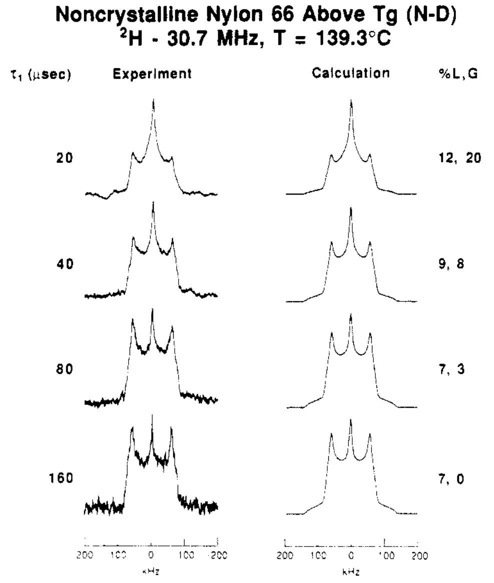

Figure 14. Experimental and calculated line shapes at 139 °C for the noncrystalline domains of the N–D-labeled polymer as a function of τ_1. The numbers next to each calculated line shape are the relative amounts of Lorentzian and Gaussian components in a three-component fit (along with the slow-exchange powder pattern).

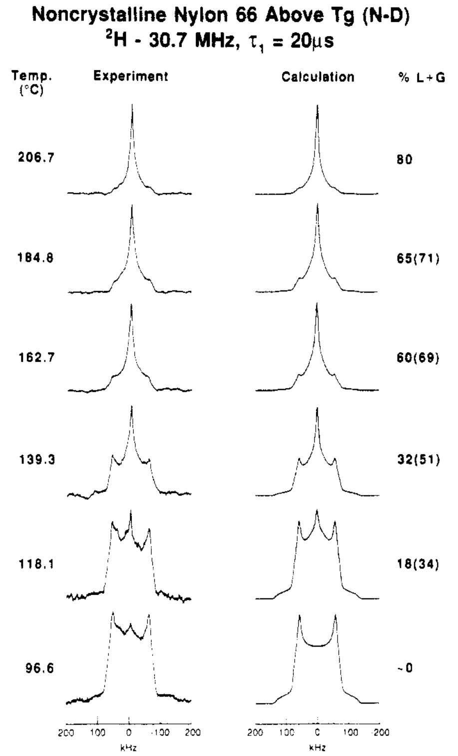

Figure 15. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of the N–D-labeled polymer as a function of temperature. The numbers next to each calculated line shape are the sum of the relative amounts of Lorentzian and Gaussian components used to fit the line shapes for τ_1 = 20 μs. The value extrapolated to τ_1 = 0 μs is given in parentheses.

bution of correlation times, is further supported by the fact that the fraction of the magnetization represented by the short spin–lattice relaxation time component remains quite close to 60% from 50 to 230 °C (Figure 12). As has been shown,[1] the fast (Lorentzian-like) and slow (nearly rigid) components of the line shape will progressively dominate as τ_1 is increased (see Figures 13 and 14).

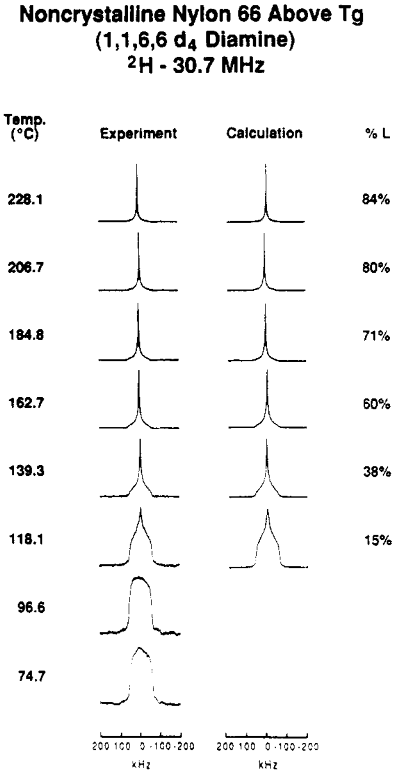

Figure 16. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of NY16NHME as a function of temperature above the glass transition temperature. The right-hand column indicates the relative fraction of the two Lorentzian components in the calculated line shape in a three-component fit (along with the broad component observed at 96 °C).

For the N–D polymer, the line shapes have been fitted to the sum of three components: slow exchange (taken to be the powder pattern observed at 97 °C), intermediate exchange (Gaussian line shape of standard deviation 25 kHz), and fast exchange (Lorentzian). The intermediate-exchange line shape is expected to be quite sensitive to details of the motion, but in the present case this component is strongly reduced in intensity by T_2 relaxation and will be severely complicated by the distribution of both rates and amplitudes of motion; thus, we have assumed that a featureless analytical form (Gaussian) will serve as a crude approximation. The analysis of the experimental line shapes (extrapolated to $\tau_1 = 0$) ignores any orientational dependence of T_2, and fitted values are given in Figure 21. The temperature dependence of the fitted values of T_2 is in accord with our expectations: the Gaussian component T_2 is quite short (25–50 μs), the fraction of slow-exchange component in the line shape decreases with increasing temperature, and the contribution of the fast-exchange component increases with increasing temperature. The T_2 of the Lorentzian component is always found to be much longer than that calculated from the line shape ($1/\pi\Delta\nu$), where $\Delta\nu$ is the full width at half-maximum line width. Good fits of the Lorentzian component are obtained with a temperature-independent $\Delta\nu$ of 10 kHz (Figures 13 and 15) which would imply a T_2 of 32 μs for a completely isotropic motion. Detailed fitting indicates that the line width increases slightly with temperature, which would appear to contradict the T_2 results (Figure 21). This apparent discrepancy is resolved by considering that the motion is not completely isotropic in that there is some residual quadrupolar coupling not averaged by the motion. This interpretation is in accord with spin alignment experiments on the amorphous phase of polyethylene, where the life-

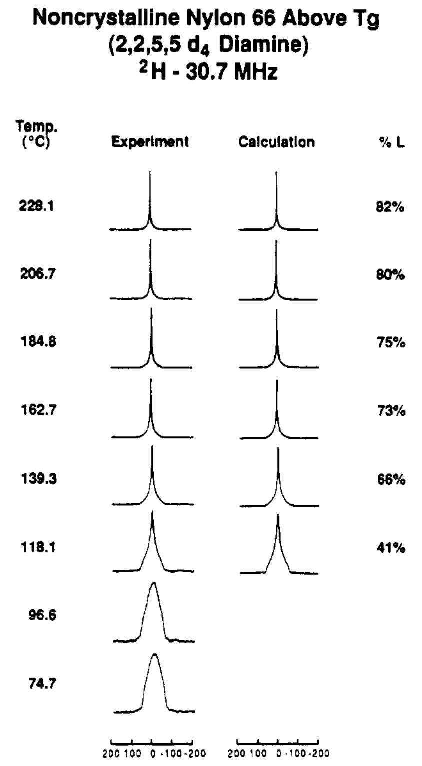

Figure 17. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of NY25NHME as a function of temperature above the glass transition temperature. The right-hand column indicates the relative fraction of the two Lorentzian components in the calculated line shape in a three-component fit (along with the broad component observed at 96 °C).

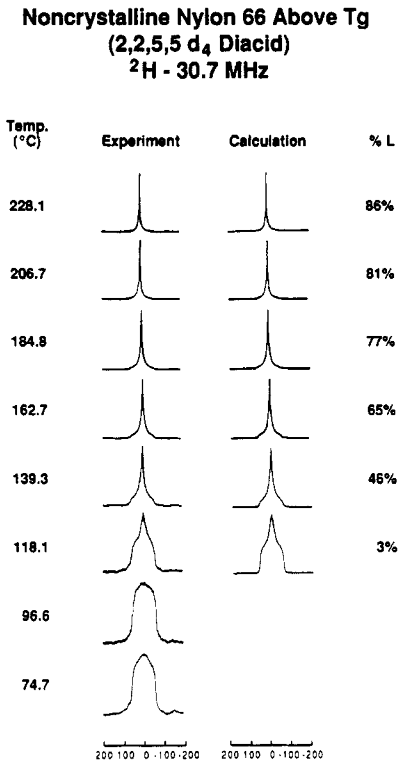

Figure 19. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of NY25COME as a function of temperature above the glass transition temperature. The right-hand column indicates the relative fraction of the two Lorentzian components in the calculated line shape in a three-component fit (along with the broad component observed at 96 °C).

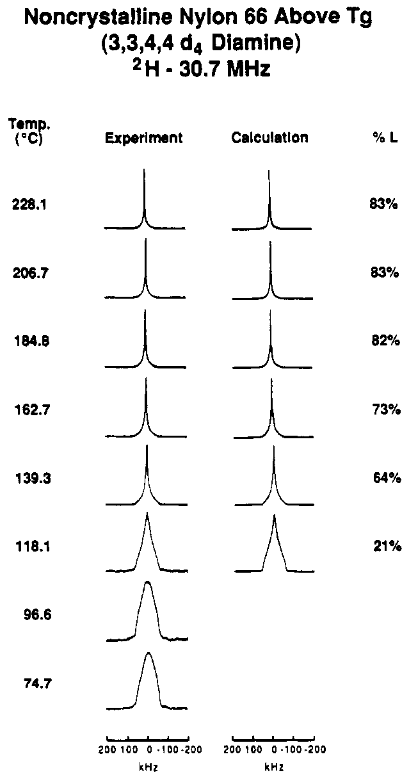

Figure 18. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of NY34NHME as a function of temperature above the glass transition temperature. The right-hand column indicates the relative fraction of the two Lorentzian components in the calculated line shape in a three-component fit (along with the broad component observed at 96 °C).

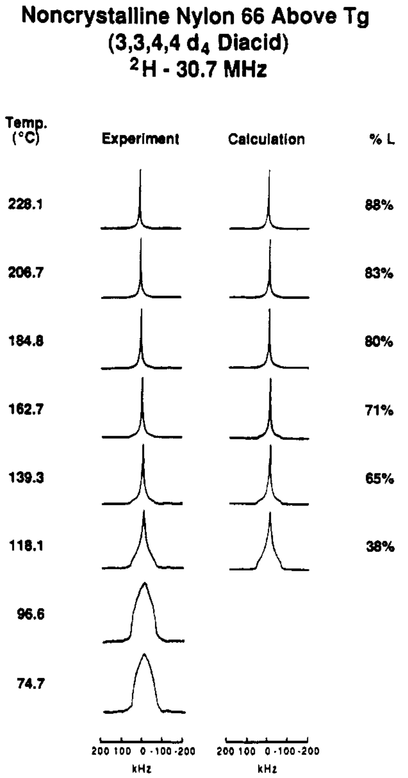

Figure 20. Experimental and calculated line shapes with τ_1 = 20 μs for the noncrystalline domains of NY34COME as a function of temperature above the glass transition temperature. The right-hand column indicates the relative fraction of the two Lorentzian components in the calculated line shape in a three-component fit (along with the broad component observed at 96 °C).

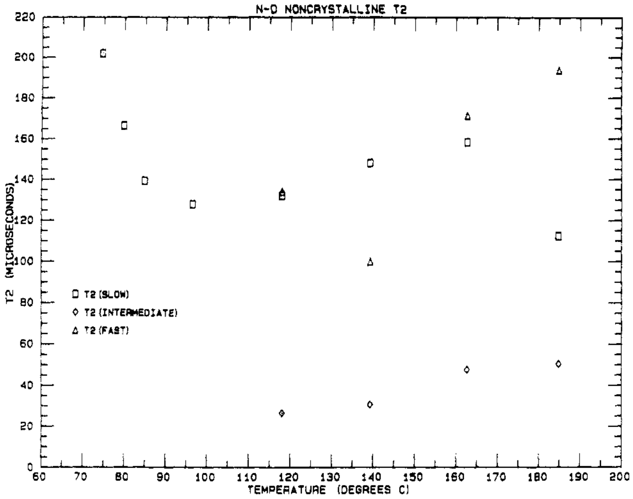

Figure 21. Temperature dependence of T_2 for each of the three components in the line shape of the N–D-labeled polymer, in noncrystalline domains, above the glass transition temperature.

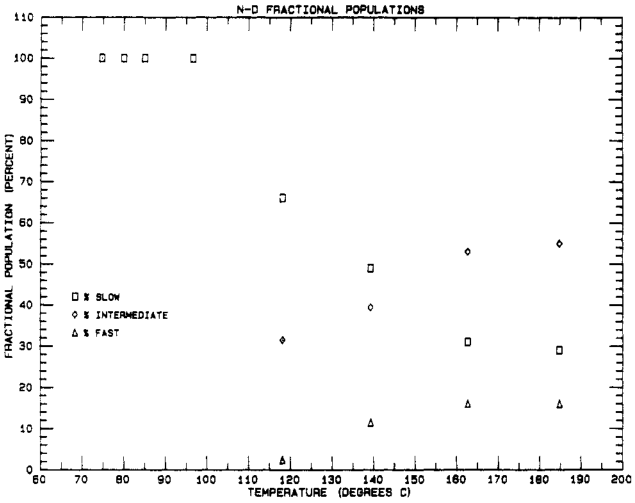

Figure 22. Temperature dependence of the populations of the three components in the line shape of the N–D-labeled polymer, in noncrystalline domains, above the glass transition temperature.

time of the averaged quadrupolar coupling is greater than 40 ms just below the melting point.[22] Additionally, the apparent slight increase of $\Delta\nu$ reflects the integration of a progressively larger fraction of the more spatially restricted segments of the amorphous domains, with increasing temperature, into the Lorentzian component. Likewise, the increase in both the fractional population and T_2 of the Gaussian component (Figures 21 and 22) indicates that there is an increasing population of segments undergoing faster, but spatially restricted, motion. Concomitant with the increase of both the Lorentzian and Gaussian components is the decrease of the fraction of the slow-exchange component (Figure 22). These observations are consistent with an inhomogeneous distribution of correlation times, but, as shown above, there must also be an inhomogeneous distribution of amplitudes of motion.

For the C–D polymers, a similar analysis of the line shapes is complicated by the complex bimodal form of the broader component of the line shape due to the presence of the γ relaxation (see above). Nevertheless, a simple analysis of the line shapes at τ_1 = 20 μs has been carried out assuming that the broad component is very similar to the amorphous line shape below the glass transition (51 °C). The intermediate- and fast-exchange components are well fit by Lorentzian line shapes with line widths of 10 and 1–2 kHz, respectively, over the entire temperature range. When compared to the N–D polymer, this implies that the motion of the methylene groups is more isotropic than that of the amide groups. This result is consistent with hydrogen bonding of the amide sites. The temperature dependence of the fractional population of the broad component is shown in Figure 23. (This may be contrasted to the results below T_g, where the fraction of constrained and free domains is essentially independent of temperature.) Although the data are scattered below 150 °C, where there are strong T_2 relaxation effects, the higher temperature data indicate that the broad component fractional population is quite similar for both C–D and N–D sites (Figure 22) above 150 °C. Although a detailed description of the molecular motion is impossible, the α relaxation process must be associated with a quasi-isotropic cooperative motion of long-chain segments containing several amide groups. This conclusion is in agreement with general concepts of the glass transition and the estimate of 15 amide groups which has been deduced from a cross-linking study.[23] The nature of the α relaxation process is in clear contrast to the noncooperative local γ relaxation (see above). Lastly, the value of the spin–lattice relaxation time of all the spins within the noncrystalline domains is about 10 ms above 150 °C, which indicates that, as below T_g, another mode of motion (libration, jump, etc.) with a correlation frequency near the Larmor frequency (not the glass transition process) dominates the spin–lattice relaxation.

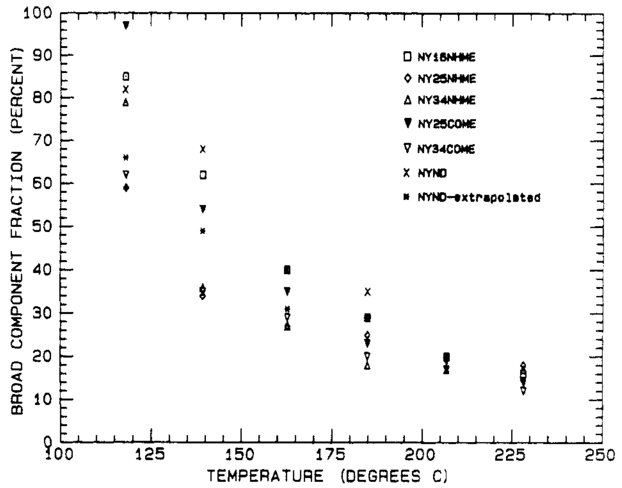

Figure 23. Temperature dependence of populations of the broad component used in the line-shape simulations for the noncrystalline domains of each of the methylene-labeled polymers above the glass transition temperature.

Results and Discussion for Wet Nylon

Spin–Lattice Relaxation. Spin–lattice relaxation times for each of the wet polymers (2 ± 0.3 wt % water) selectively deuterated at each methylene group are shown in Figures 24 and 25. The spin–lattice relaxation times for the wet polymers are quite similar to those found for the dry polymers[1] with the only difference being that the very shallow minima observed in the dry polymer at ~0 °C (γ-process) and ~150 °C (α-process) are very diffuse in the wet polymer. Values of the amplitudes of magnetization associated with the more slowly relaxing spin–lattice relaxation time component, in a two-component fit, are near ~50% in the interval −50 to 50 °C and are near 40% in the interval 50–230 °C. Thus, this method of discriminating magnetization arising from crystalline and noncrystalline domains is reasonably effective for the

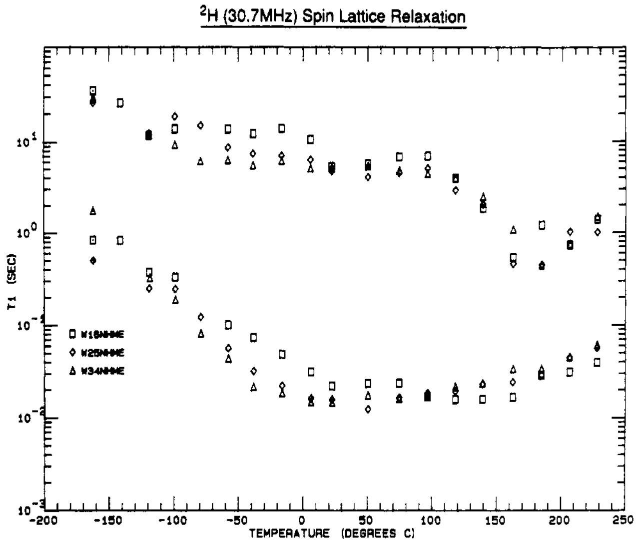

Figure 24. Temperature dependence of the spin-lattice relaxation time, for a two-component fit, for each of the three polymers (containing 2.0 ± 0.3 wt % water) labeled in the HMDA moiety.

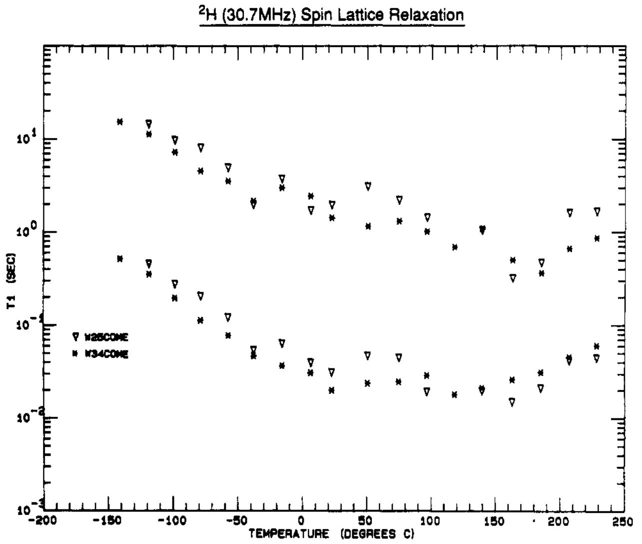

Figure 25. Temperature dependence of the spin-lattice relaxation time, for a two-component fit, for each of the two polymers (containing 2.0 ± 0.3 wt % water) labeled in the adipoyl moiety.

wet polymer also. This result is in accord with the belief that either the diffusion of water into nylon crystals is very slow or more likely that the equilibrium concentration is very low.[7,24] Observation of similar data for the N-D polymer is precluded by rapid hydrogen/deuterium exchange with the introduction of water.

C-D Motion. Figures 26–30 illustrate comparative line shapes for magnetization arising from specific methylene groups within noncrystalline domains of wet and dry nylon 66 polymers. The line shapes are virtually identical below -50 °C, differ slightly in the temperature range -50 to 50 °C, and are vastly different above 70 °C. This latter point is best exemplified by the presence of a very narrow component in the line shape of the wet polymer at and above 75 °C; whereas this same behavior is not observed in the dry polymer until 118 °C. Similar behavior is manifested in the T_2 data shown in Figure 31 in that the wet polymer appears to have a weak minimum near 70 °C while this feature is not observed for the dry polymer until ~100 °C.

The appearance of a sharp Lorentzian component in the line shape associated with the noncrystalline domains in the wet polymer, as in the dry polymer, must be associated with segments undergoing essentially isotropic molecular motion that is fast on the time scale of the line shapes (~10^5 Hz). This process is the onset of the glass transition or α relaxation.[2] The appearance of this component in the wet polymer line shapes at a temperature that is ~40 °C lower than that found for the dry polymer is in good agreement with the observed decrease of the glass transition with the introduction of ~2% water.[2,7] In addition, the temperatures at which the narrow components are observed in both dry and wet polymer (118 and 75 °C, respectively) are consistent with the maxima observed in dielectric loss at 10^5 Hz.[23] The T_2 data of Figure 31 also reflect this same behavior at slightly lower temperatures (the decrease of T_2 begins at 50 and 20 °C in the dry and and wet polymers, respectively) because the rate of the motion, although not sufficiently rapid to average the line shapes, is fast enough to shorten T_2.[25]

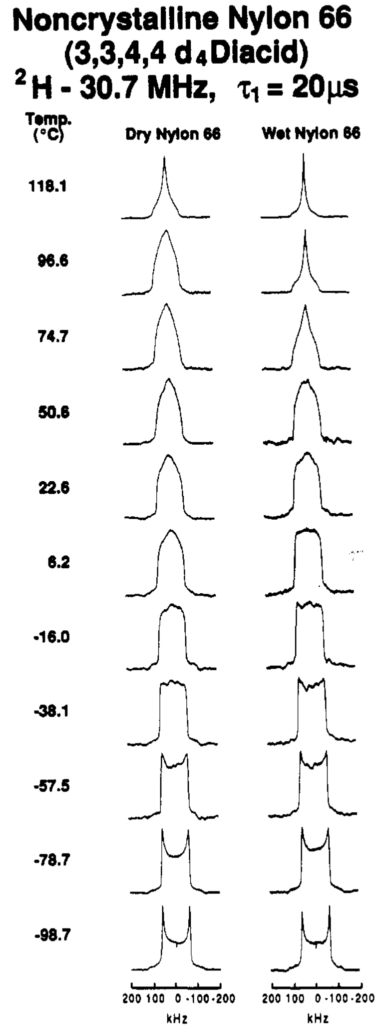

Figure 26. Comparative experimental line shapes for the noncrystalline fraction of dry and wet NY16NHME as a function of temperature.

Below -50 °C, there are no detectable differences between the dry and wet nylon polymers for either of the line shapes, T_1 or T_2. Therefore, the γ relaxation description developed for the dry polymer must also be applicable to the wet polymer. In the temperature interval of -50 to 50 °C, the line shapes (Figures 26–30) are very similar for both the dry and wet polymer and indicate that the γ relaxation is present in the wet polymer and is responsible for the motional averaging below 50 °C. Detailed comparison of the wet and dry polymer line

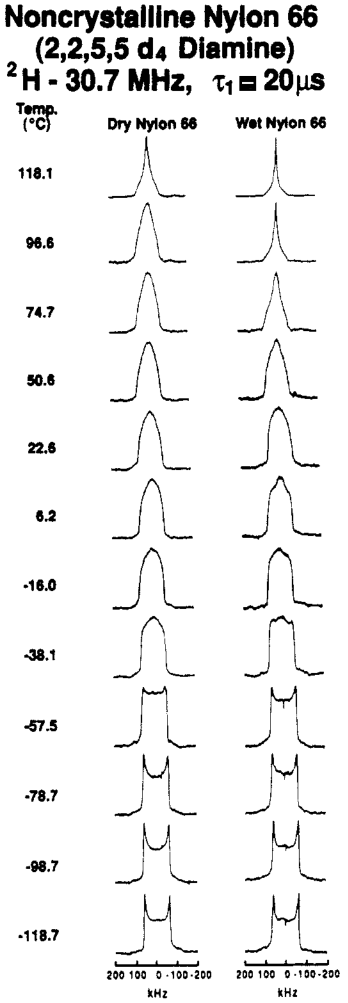

Figure 27. Comparative experimental line shapes for the noncrystalline fraction of dry and wet NY25NHME as a function of temperature.

shapes indicates that there appears to be a *slight* reduction in the amount of motional averaging in the wet polymer. This slight reduction might be thought to be correlated with the reduction in strength of the γ relaxation as observed with other methods; however, the rate of the γ relaxation has been shown to increase slightly upon the addition of water,[2,7,26] thus making it quite unlikely that this correlation is valid. This slight *apparent* reduction in motional averaging is most likely due to T_2 relaxation effects,[1] which cause intensity losses in the central region of the line shape. Indeed, the T_2 relaxation time of the wet polymer is substantially shorter than that observed for the dry polymer in the temperature interval -50 to 50 °C (Figure 31). Additionally, the T_2 is never observed to approach the value (200 μs) that would be observed in the fast motion limit of the γ relaxation.[1] The reduction of the T_2 below 0 °C cannot be due to the glass transition process, because at 2 wt % water the T_g is depressed by only 40 °C. The observed reduction of the T_2 relaxation time of the wet polymer in the temperature interval -50 to 0 °C must be due to the presence of an intermediate relaxation. This intermediate process is the β relaxation and has been shown by several techniques to be essentially absent in carefully dried nylon and to increase in strength with increasing water content; the frequency of this relaxation is in the range 100 Hz to 10 KHz in the temperature range -50 to 0 °C.[2,7,26] This process must be responsible for the observed reduction in T_2 in this temperature interval but is sufficiently slow so as to not affect any motional averaging of the line shapes. These results indicate that the β relaxation must involve all of the methylene groups, but no specific model of the geometry of the motion can be deduced. Although an increase of the water concentration would further increase the strength of the β relaxation, the concomitant depression of the temperature of the α relaxation would mask the β process at the relatively high frequencies used in these experiments ($\nu_Q \sim 10^5$ Hz).

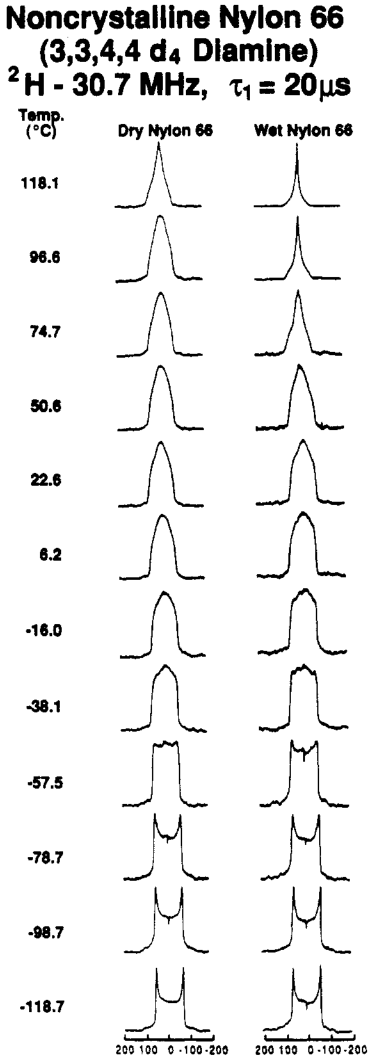

Figure 28. Comparative experimental line shapes for the noncrystalline fraction of dry and wet NY34NHME as a function of temperature.

Summary

First, as described in the previous paper,[1] the magnetization attributable to crystalline and noncrystalline domains for all of the C–D sites and the N–D sites may be effectively separated by spin–lattice relaxation time discrimination. Furthermore, the present results indicate that the motion responsible for this discrimination is a small-angle fluctuation (either diffusive or jump like, mode I) that occurs with a rate near the Larmor frequency at all temperatures above ~ -50 °C for both the "constrained" and "free" amorphous populations.

Second, the amide N–D motion below T_g is characterized as an inhomogeneous distribution of small-angle rapid fluctuations (librations); at 97 °C, the N–D bond librates ~ ±10° at a mean correlation frequency of 5×10^8 Hz. Above T_g, the α-process is indicated by the appearance of a narrow component in the line shape attributable to

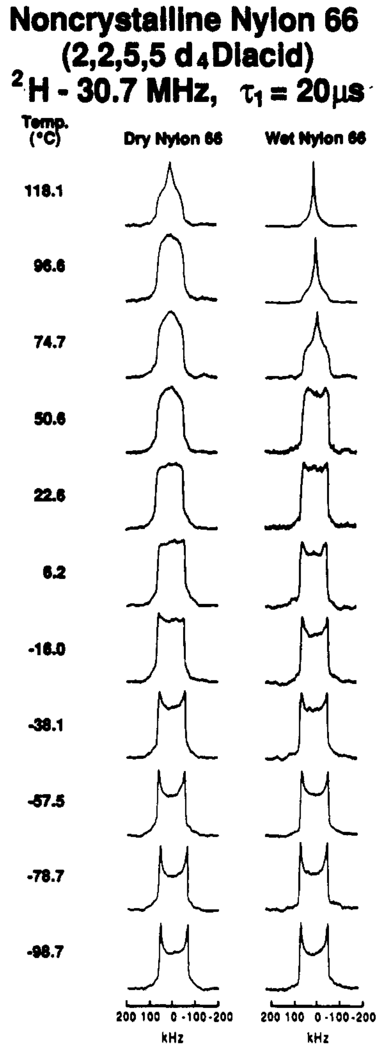

Figure 29. Comparative experimental line shapes for the noncrystalline fraction of dry and wet NY25COME as a function of temperature.

sites undergoing nearly isotropic motion. The fraction of sites undergoing nearly isotropic motion grows with temperature and is near 80% at 207 °C; this result reflects not only the broad distribution of amplitudes of motion but also of rates that must exist for the N–D sites above T_g. Furthermore, these results indicate that there are N–D sites in the amorphous phase which are substantially hindered even quite close to the crystalline melting point.

Third, the C–D sites below T_g reflect the presence of two distinct environments (*not a broad distribution of correlation times*), and the fractional populations are essentially temperature independent. The smaller population only exhibits mode I motion at all temperatures below T_g. Mode I motion is characterized as an inhomogeneous distribution of small-angle fluctuations (librations). This motion is rapid ($1/\tau > 10^7$ Hz) above −50 °C, and the rate decreases as the temperature is lowered. The major fraction exhibits both mode I and mode II motion. Mode II motion is modeled as a discrete trans–gauche jump, and the rate and activation energy of this process agree with previous dielectric and mechanical relaxation results for the γ relaxation. The populations and librational parameters ($\Delta(\Delta\theta)$ and $\Delta\phi$) reflect the spatial inhomogeneity of the amorphous phase and are essentially temperature independent. Moreover, the population exhibiting only librational motion ("constrained") may tentatively be associated with interfacial or strongly hydrogen bonded segments in the semicrystalline polymer, whereas the population exhibiting both librational and internal rotation motion ("free") may be unhindered amorphous polymer. In contrast to this result, the parameters which approximately reflect the mean value of the amplitude of libration for both populations ($\Delta\theta$, $\Delta\theta_0$) are temperature dependent and differ for each C–D

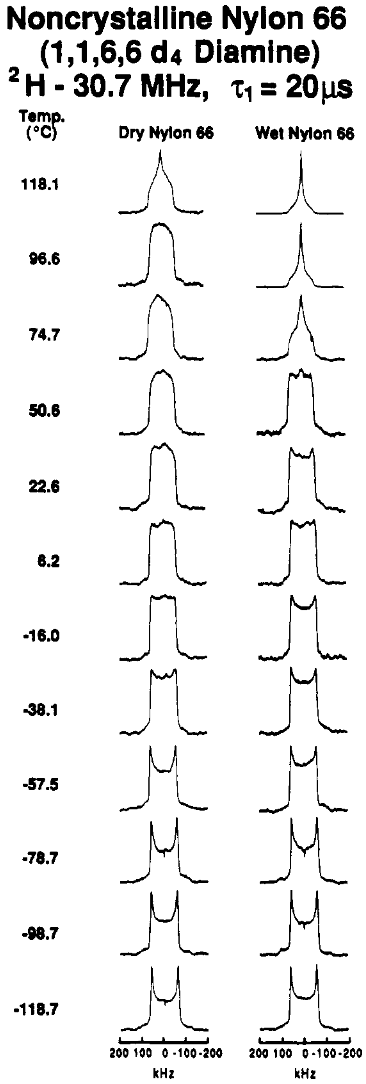

Figure 30. Comparative experimental line shapes for the noncrystalline fraction of dry and wet NY34COME as a function of temperature.

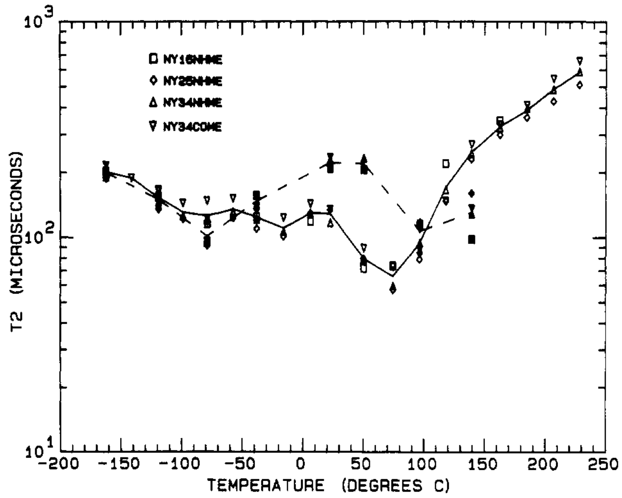

Figure 31. Temperature dependence of T_2 for both dry (filled symbols) and wet polymer (open symbols) for each of the C–D-labeled polymers.

site; the C–D sites α to the amide linkage exhibit smaller amplitude librations reflecting the constraint imposed by the relatively rigid adjacent amide sites. Note that in the crystalline domains all methylene groups within each moiety exhibit essentially identical motion.

Fourth, for the C–D sites above T_g, as for the N–D sites, the α-process is indicated by the appearance of a narrow component in the line shape attributable to sites undergoing nearly isotropic rapid motion. This component in these line shapes is even narrower than that for the N–D sites at the same temperature, indicating that the motion is even closer to being isotropic. The fraction of sites undergoing nearly isotropic rapid motion grows with temperature and is near 80% at 207 °C; this result is very similar to that found for the N–D sites and indicates that the process responsible for the temperature dependence of the line shapes and T_2 involves both C–D and N–D in a quasi-isotropic motion and may be identified with the α relaxation. This process involves a broad distribution of both rates and amplitudes of motion. Also, as for the N–D sites, there exists a fraction of C–D sites in the amorphous phase which are substantially hindered even quite close to the crystalline melting point.

Fifth, the presence of 2 ± 0.3 wt % water in the polymer appears to have little effect upon the γ process. The α process is depressed by ~40 °C, consistent with mechanical and dielectric relaxation results. Additionally, the T_2 relaxation data for the C–D sites indicate the presence of an intermediate relaxation in the temperature interval -50 to 50 °C, and this observation is consistent with the β-process. The data here do not allow the identification of a specific trajectory of motion for this relaxation, only that it involves all of the methylene groups. This intermediate process is not seen in the dry polymer.

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References and Notes

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