Characterization of Structure and Morphology in Nylon 6 by Solid-State ^{13}C and ^{15}N NMR

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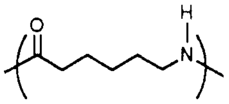
ABSTRACT: The α, γ, and amorphous phases of nylon 6 have been characterized by solid-state ^{13}C and ^{15}N NMR. This includes the first solid-state NMR results reported for an ^{15}N-labeled nylon 6 polymer. Several NMR approaches have been applied in order to provide a clear characterization of the NMR spectra. The observed ^{13}C and ^{15}N chemical shifts are discussed in terms of a combination of structural interactions including hydrogen bonding, hyperconjugation, and chain packing. Some evidence is presented which suggests that interchain hydrogen bonding is stronger in the γ phase than in the α phase, in spite of the fact that the α phase is more thermodynamically stable. Structure/chemical shift relationships are also used to provide new insights into the nature of the amorphous phase.

Introduction

The polyamide "nylon 6" (N6) is an important polymeric material[1] with applications ranging from carpet and automotive parts to intimate apparel. The structure of N6 is given below. In spite of extensive study for nearly



5 decades, many fundamental questions persist concerning the structure and behavior of this material.

Solid-state NMR is quickly becoming one of the more powerful and versatile tools available for the study of polymer structure, morphology, and dynamics.[2,3] This strength has led to some recent interest in applying NMR to nylon 6 and nylon 6 composites.[4-10] We have been using ^{13}C and ^{15}N NMR for some time to characterize the structure, morphology, and dynamics of nylon 6 materials. The purpose of this manuscript is to present many of these results and lay a detailed groundwork for future studies. The results presented here were obtained from well-characterized samples and have been correlated with infrared and X-ray diffraction studies. In addition, we present the results from the first solid-state ^{15}N NMR studies of an ^{15}N-enriched nylon polymer. Finally, a number of structure/shift relationships are discussed and used to provide new insights into the structure of the amorphous phase.

Experimental Section

Samples. Nylon 6 was synthesized by anionic polymerization of ϵ-caprolactam as described in detail elsewhere.[11] The sample was found to have a weight-average molecular weight of 14 900 with a polydispersity of 2.8. All samples were analyzed under ambient conditions with water contents of typically 6%. The effects of water absorption on the NMR spectra of nylon 6 will be discussed in a subsequent publication. The sample of low crystallinity was generated by melting the original ^{15}N labeled powder at 280 °C in a Wabash 50 ton press and immediately quenching the resulting film in ice water. The sample high in γ crystallinity was prepared in a fashion similar to that described elsewhere.[12] The original finely ground polymer was stirred in a 1.1 M aqueous solution of potassium iodide and iodine overnight. The finely divided black product was filtered, washed with water, and air dried. This material was then stirred in a solution of 1 M sodium thiosulfate for several hours, filtered, and air dried.

NMR Spectroscopy. Solid-state ^{13}C and ^{15}N NMR spectra were acquired at 75.3 and 30.3 MHz, respectively, on a Chemagnetics CMX300 NMR spectrometer. All of the spectra presented in the text were obtained from ^{15}N-labeled nylon 6 samples. Data were obtained under magic-angle spinning (MAS) conditions using standard cross-polarization (CP) and single-pulse (BD, Bloch decay) techniques.[13-15] Other experimental details pertaining to the choice of NMR pulse sequences are provided in the text. The magic angle was adjusted to within 0.1° by using the ^{79}Br spectrum of KBr.[16] Where appropriate, spectra were acquired by using a 0.8 ms contact time, pulse delays of 1-3 s, and T_1 delays in the CPT1 sequence of 10-30 s (see below). Solution-state ^{13}C and ^{15}N NMR spectra were obtained at 100.4 and 40.4 MHz, respectively, on a Varian XL400 NMR spectrometer. All spectra were externally referenced relative to TMS (^{13}C, 0 ppm) or NH_3 (^{15}N, 0 ppm).

Background

Nylon 6 is known to exist in two crystalline forms. The most thermodynamically stable structure is called the alpha (α) phase and consists of molecules in an extended-chain conformation with hydrogen bonds between antiparallel chains.[17] The second form is known as the gamma (γ) phase. In this structure the molecules form pleated sheets in which hydrogen bonds exist between parallel chains.[18] Schematic illustrations based on the original structural work of Bunn[17] and Arimoto[18] are given in Figure 1. Refinements to the α-crystalline structure have also been reported.[19] In Figure 1, the solid circles represent carbon atoms, the shaded circles represent oxygen, and the open circles represent nitrogen. Very little is known about structure in the amorphous phase.

One of the strengths of NMR is its versatility. By changing the NMR experiment, or pulse sequence, it is possible to dramatically alter the observable being detected. In this fashion, NMR experiments can be designed to probe molecular structure,[2,3] dynamics,[2,3,20] orientation,[2,3,21] and so on. In this paper, we have used three experiments to clarify the NMR spectra of nylon 6. Each has been described in detail elsewhere[2,3,14,15,22] and will only be briefly highlighted here. The first is a single-pulse experiment identical with that done in solution but with the addition of magic-angle spinning (MAS) and high-power proton decoupling. This experiment will hereaf-

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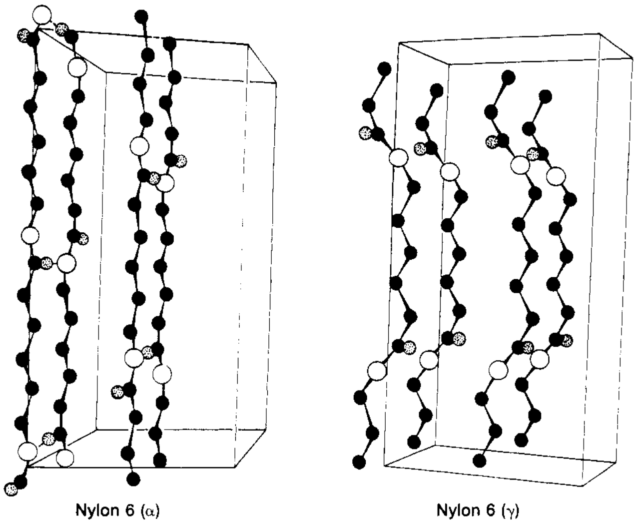


Figure 1. Schematic illustration of the α and γ crystalline forms of nylon 6.

ter be referred to as BD/MAS (Bloch decay/magic-angle spinning). By selecting an appropriately short repetition time, this experiment can be used to detect only the most mobile nuclei, i.e., those in the amorphous phase. The utility of this experiment for observing the amorphous phase of nylon 6 has been previously demonstrated.[4] The second experiment, referred to as CP/MAS (cross-polarization/magic-angle spinning), is commonly used to observe the entire semicrystalline system and accounts for almost all of the previously reported nylon 6 work.[4-10] The final experiment, hereafter referred to as CPT1, is one that can be used to observe only the crystalline fraction of the polymer.[22] This paper represents the first application of this method to nylon 6. We have judiciously used each of these experiments to "deconvolute" the often complex NMR spectra of nylon 6. This had enabled us to unequivocally assign specific peaks to the three phases of nylon 6. In some cases, these assignments differ from those previously reported.

The NMR characterization of structure and morphology in nylon 6 will be illustrated by using three samples. These have been prepared to be rich in amorphous, α-crystalline, and γ-crystalline phases. Based on our own NMR results, as well as supporting infrared and X-ray diffraction studies, it has been determined that the "highly amorphous" sample contains low fractions of α and γ phases. The sample "high in α crystallinity" contains a substantial amorphous fraction but no γ content. Similarly, the sample "high in γ crystallinity" was determined to contain a substantial amorphous fraction but no α content. Quantitation of nylon 6 phase content by NMR has been reported elsewhere[4,9] and will not be treated here.

Results and Discussion

^{13}C CP/MAS NMR spectra of nylon 6 samples high in amorphous, α, and γ content are given in Figure 2. Peaks marked with an asterisk are due to spectral features called spinning sidebands and should be ignored. Recall from the discussion above that the CP/MAS experiment observes all of the phases in the semicrystalline system. Note that there are dramatic differences in the appearance of the spectra as the level of each phase varies. This clearly demonstrates, as previously reported,[4-8] that ^{13}C NMR is sensitive to the conformational differences that exist between the three phases. However, the assignment of the various peaks to each phase is not straightforward and requires a more thorough investigation than simple inspection.

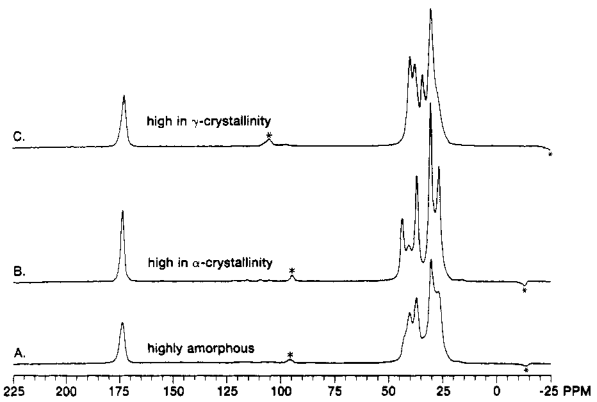


Figure 2. ^{13}C CP/MAS NMR spectra of nylon 6 samples that were (A) predominantly amorphous, (B) high in α crystallinity, and (C) high in γ crystallinity.

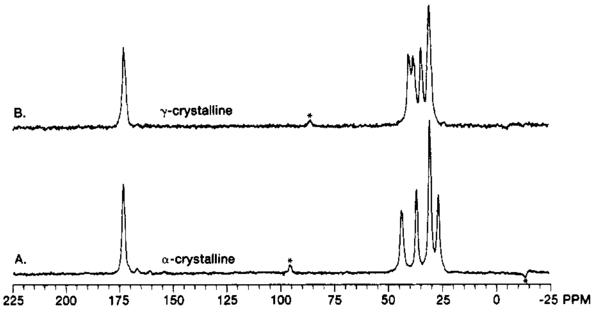


Figure 3. ^{13}C NMR (CPT1) spectra that discriminate in favor of the crystalline phase (see text) for samples that were (A) high in α crystallinity and (B) high in γ crystallinity.

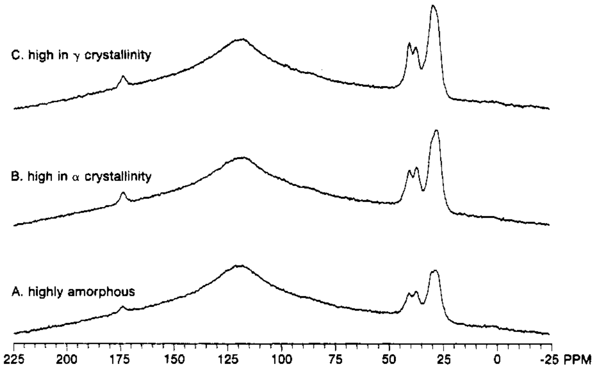


Figure 4. ^{13}C NMR (BD/MAS) spectra that discriminate in favor of the amorphous phase (see text) for samples that were (A) predominantly amorphous, (B) high in α crystallinity, and (C) high in γ crystallinity.

Recall from the discussion above that spectra characteristic of only the crystalline fraction can be obtained by using the CPT1 experiment.[22] Given in Figure 3 are spectra obtained in this manner for the samples rich in α- and γ-crystalline phases. Note that they are "simpler" than the analogous spectra in Figure 2B,C. These results clarify the interpretation of Figure 2 by identifying those peaks specific to the crystalline phases.

By using the BD/MAS experiment and a repetition time far shorter than the T_{1C} of the α and γ phases, it is possible to obtain spectra of only the amorphous fraction in each sample. This is illustrated in Figure 4. In the BD/MAS experiment, a broad background signal from probe material appears at roughly 110 ppm and should be ignored. Note that all three spectra are essentially the same. This suggests that the structure of the amor-

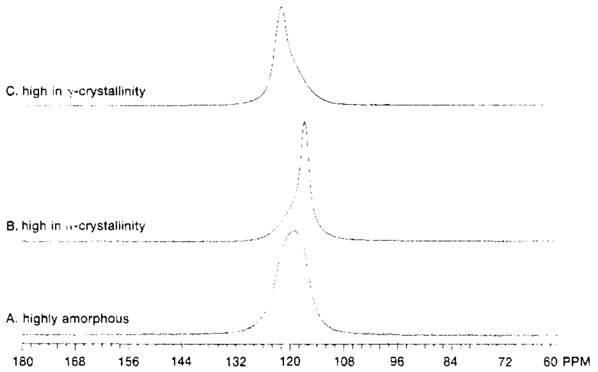


Figure 5. ^{15}N CP/MAS NMR spectra of nylon 6 samples that were (A) predominantly amorphous, (B) high in α crystallinity, and (C) high in γ crystallinity.

phous phase (as measured by BD/MAS NMR) is not sensitive to the composition of the crystalline phases in the sample. Note also that the carbonyl peak is diminished in intensity relative to that from the other carbons along the chain. This is due to the longer T_{1C} of the carbonyl relative to the rest of the chain, as expected. From these spectra it is possible to determine the chemical shifts for the amorphous phase of nylon 6. Unfortunately, the most upfield portion of the spectrum (30–25 ppm) contains relatively broad lines, making accurate assignment difficult. However, BD/MAS experiments[23] carried out at elevated temperatures (above T_g) reveal a substantial line narrowing with no changes in peak position and permit an accurate peak assignment for the amorphous phase.

An important part of the polyamide structure is interchain hydrogen bonding. The extent and strength of this bonding plays a pivotal role in determining the intermolecular interactions that govern the physical properties and behavior of the polymer. An excellent way to probe the nature of this bonding is to directly study the NH site. This can be done by using ^{15}N NMR. Unfortunately, this is a difficult experiment due, in part, to the low natural abundance of ^{15}N (0.37%). However, solid-state ^{15}N NMR spectra of nylon 6 at natural abundance levels have been reported.[9,10] Mathias and coworkers[9,10] have shown that ^{15}N NMR is sensitive to phase structure and composition in several nylons. Unfortunately, these results are, in some ways, hampered by problems with low signal to noise. Since the samples used in this study were ^{15}N labeled, we were able to obtain high-quality ^{15}N spectra of the amorphous, α, and γ phases. The results are given in Figure 5. The ^{15}N spectra in Figure 5 were taken from the same polymers used to generate the ^{13}C spectra in Figure 2. Note that the ^{15}N spectra are different, revealing that the nitrogen environments in each phase are also different. The samples high in α and γ crystallinity each contain a sharp peak and a broad shoulder, presumably due to crystalline and amorphous nitrogens. This interpretation was confirmed by carrying out the CPT1 experiment and observing ^{15}N. These results are given in Figure 6.

By applying several NMR "strategies", we have shown that it is possible to unequivocally assign specific ^{13}C and ^{15}N NMR peaks to the three phases of nylon 6. The NMR "selection" of phases was based on gross differences in spin–lattice relaxation behavior. A more detailed examination of this behavior may reveal that similar approaches are capable of selectively observing more tenuous structural features such as chain folds or regions of an "ordered amorphous" structure. Experiments such as this are under way. The NMR phase assignments have also been empirically confirmed by using a number of samples with varying levels of crystallinity.

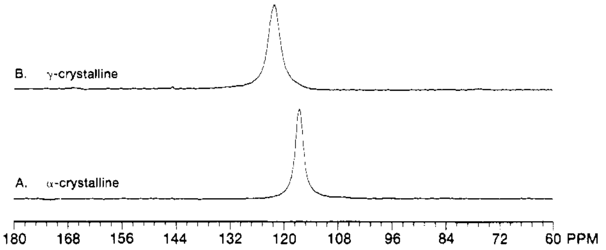
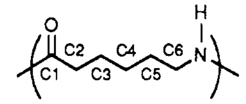


Figure 6. ^{15}N NMR (CPT1) spectra that discriminate in favor of the crystalline phase (see text) for samples that were (A) high in α crystallinity and (B) high in γ crystallinity.

Table I
^{13}C and ^{15}N NMR Chemical Shift Assignments for Nylon 6



phase	^{13}C1	^{13}C2	^{13}C3	^{13}C4	^{13}C5	^{13}C6	^{15}NH
α[a]	173.4	36.7	26.5	30.4	30.4	43.6	116.5
γ[a]	173.0	37.8	30.1	30.1	34.1	39.9	121.8
amorphous[b]	174.5	36.9	26.2	27.4	30.0	40.3	119.1
solution[c]	177.8	37.2	26.4	27.1	29.5	40.7	122.7

[a] ^{13}C results taken from peak maximas in CPT1 crystalline phase discrimination experiment; see text. [b] ^{13}C results taken from peak maximas at 110 °C in a BD/MAS amorphous phase discrimination experiment; see text. [c] Dilute trifluoroethanol solution.

^{13}C and ^{15}N NMR peak assignments for the α, γ, and amorphous phases of nylon 6 are summarized in Table I. For comparative purposes, ^{13}C and ^{15}N NMR spectra were also acquired from solutions of dilute trifluoroethanol. The solution-state assignments are identical with those recently reported[24] from one- and two-dimensional NMR methods. The tentative assignments for the solid phases are made by assuming the same shift trends in all phases. In order to adequately understand the chemical shifts in terms of local polymer structure, it is necessary to consider a number of effects such as conformation, hydrogen bonding, γ-gauche interactions, and crystallite packing.

As discussed above, the nature of the hydrogen bonding in polyamides plays a key role in determining their physical properties. There are, potentially, two major types of hydrogen bonding in these systems, associated with segment–segment and segment–solvent interactions. Hydrogen bonding creates a delocalization of electronic charge, which results in a net decrease in electron density at both the carbon CO and nitrogen NH sites. The result is that each nucleus becomes deshielded and the ^{13}CO and ^{15}NH NMR shifts are expected to move downfield. We begin by considering hydrogen bonding in light of the ^{15}N NMR data given in Table I. It has been shown[25-27] that for polyamides in solution, hydrogen bonding through either the NH or CO results in a downfield ^{15}N shift and that the ^{15}N shifts progress downfield as the strength of the hydrogen-bonding solvent increases. Using this rationale, one would expect a more downfield ^{15}N shift to be indicative of increased hydrogen bonding. The most downfield ^{15}N shift in Table I is for nylon 6 in trifluoroethanol (TFE) solution. Here, we are dealing with the case of segment–solvent hydrogen bonding. TFE is a stronger hydrogen donor than would be a neighboring amide chain and it is possible for more than one TFE molecule to solvate the carbonyl group. Thus, is not surprising that the amide nitrogen in solution would result in the most downfield shift.

It is possible to extend these arguments to the solid phases where hydrogen bonds exist between chains. The data in Table I suggest that the strength of hydrogen bonding is greatest in γ, followed by amorphous and then α nylon 6. This same conclusion has also been inferred from infrared and X-ray data.[29] This is a surprising result since it suggests that the γ and amorphous phases are more strongly hydrogen bonded than the more thermodynamically stable α-structure. This would imply that the thermodynamic stability of the α-phase relative to the γ phase arises from interactions other than (or in addition to) hydrogen bonding. Plausible explanations for this include chain packing effects and/or preferred van der Waals and electrostatic interactions. We are continuing to probe the relationship of hydrogen bonding and other packing effects in a number of related polyamides.

We now turn to a discussion of the ^{13}C NMR shifts in terms of hydrogen bonding. By extending the arguments used for the ^{15}N shifts, one would predict that the carbonyl carbon of the γ phase would be shifted downfield relative to the α phase. In fact, there is little differences between the two frequencies. However, in the amorphous phase and in TFE solution (where segment–solvent hydrogen bonding occurs), there is an observed downfield ^{13}CO shift. One explanation that accounts for the apparent discrepancy in the α and γ ^{13}CO shifts is that other factors are compensating for the hydrogen bonding effect on the ^{13}C shifts in the crystalline phases of nylon 6. Several possibilities exist including, among others, hyperconjugation and chain packing effects.

A simple analysis of the ^{13}C NMR shifts in terms of nylon 6 structure is not straightforward. Note from Table I that the ^{13}C shifts for carbons C3, C5, and C6 are substantially different in the α and γ phases. These differences undoubtedly reflect the structural differences between the phases. Okada[7] has proposed that hyperconjugation[30] can be used to account for the deshielding of carbons C3 and C5 in the γ phase relative to the α phase (Table I). In the α phase, the methylene chain is fully extended (Figure 1). However, in the γ phase the amide group is rotated out of plane so that the C2–C3 σ bond can overlap with the π orbitals of the carbonyl group, allowing a transfer of electron density into the carbonyl. This should qualitatively deshield C3 and shield C1. The shielding of C1 might compensate for the deshielding expected from hydrogen bonding. Okada[7] applied the same argument to explain the deshielding of C5 through hyperconjugation with the p orbital of the amide nitrogen. Hyperconjugation would not seem to apply here since the nitrogen p orbital is filled and one would not expect effective electron transfer to occur from the C6–C5 σ bond toward the amide group. Further, hyperconjugation would increase the charge density at nitrogen and would be expected to cause a shielding effect on the ^{15}NH chemical shift. This is opposite to the observed result (Table I). Thus, hyperconjugation appears to be an attractive explanation for the deshielding of γ-C3 but not for the deshielding at γ-C5. Thus, we are still left seeking adequate explantations for the changes at C5 and C6. Simple electronic effects also apparently do not account for these differences. Semiempirical (MNDO) and ab initio (Gaussian 86, 6-31g basis set) calculations carried out[31] on model alkyl amides reveal no trends that correlate directly with the observed differences between the α and γ phases of nylon 6. It is possible that intermolecular crystal forces are producing some of the observed shifts. Experiments designed to probe this possibility are planned.

An obvious benefit of a clear understanding of the chemical shift determining interactions of polyamides is the potential of modeling amorphous phase structures. Although it is difficult at this time to characterize this phase with total confidence, it is possible to gain some new insight into the "average" amorphous structure.[23] Except for the carbonyl carbon where differences in hydrogen-bonding effects are expected, the chemical shifts of the carbon resonances are very similar for solution and the amorphous phase. This is reasonable only if local intramolecular energetics are determining the average conformations for the polymer chain in both phases. Recall that the α structure is in an extended chain conformation while the γ phase has the amide group rotated out of the plane of the methylene chain. The differences in chemical shift for C3, C5, and C6 between the α and γ phases apparently reflect this change. Note from Table I that the chemical shifts for C3 and C5 are essentially the same in the α and amorphous phases but differ from the γ phase. This suggests that the amorhous chains prefer an extended conformation about the amide moiety. In addition, we can find no evidence for a "γ-gauche" effect for the methylene carbons like that observed in vinyl polymers.[32] If a γ-gauche interaction were causing the shielding of C6 in the amorphous phase, C3 should also be shielded, which is not observed. Similarly, the shielding of C4 in both solution and the amorohous phase relative to either crystalline phase cannot be attributed to a γ-gauche effect. Instead, this shift suggests the removal of some deshielding effect in the crystal, possibly related to packing. We are continuing to probe the structure/chemical shift relationships of these and similar systems in an attempt to provide additional insights into the structure of crystalline and amorphous polyamides.

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Comparison of Rotating Frame Spin Relaxation and Self-Diffusion in Polyethylene and Poly(ethylene oxide) Melts

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ABSTRACT: The spectrum of rotating frame relaxation times ($T_{1\rho}$) has been obtained for poly(ethylene oxide) (PEO) melts over a range of molar masses. Comparison with the $T_{1\rho}$ spectrum for polyethylene (PE) indicates that the local motion anisotropy is considerably lower in PEO and that tube renewal occurs more rapidly. In both polymer melts, semilocal motion is observed to be approximately molar mass independent. Self-diffusion measurements in PE and PEO melts yield tube renewal time constants consistent with those measured directly via $T_{1\rho}$ dispersions.

Introduction

The fluctuating dipolar interactions experienced by nuclear spins imbedded in polymeric liquids result in a spin relaxation spectrum characteristic of the molecular dynamics. In favorable circumstances it is possible to use this spectrum to probe the hierarchy of motions present in polymer melts.[1-3] In particular we shall be interested in polymer chains of sufficient length to suffer physical entanglement[4] in which this hierarchy is characterized by the Doi-Edwards[5] and de Gennes[6] models. On an increasing time scale these motions are the local segmental motion, the semilocal curvilinear diffusion, and the tube renewal relaxation. There are two principal conditions for observing the hierarchy. First, the rapid segmental reorientation should have a residual anisotropy which therefore leaves a spin correlation order remaining to be modulated by slower motions.[1] Second, the spin relaxation should be observed by using a method that is sensitive to spectral components in the region of interest. The first condition confines the method to melts where the proximity of intermolecular segments inhibits free isotropic motion. The second requires that we have the facility to vary the separation of the nuclear Zeeman levels in order to probe the dipolar spectral density. Such variation occurs, for example, in field cycling T_1 experiments, a method employed by Kimmich and co-workers. Alternatively, the method of rotating frame relaxation[7] allows us to vary the Zeeman splitting of spins in the frame of reference of an rf field adjustable strength.

In an earlier paper, the influence of polymer melt dynamics on rotating frame relaxation of nuclear spins was described and the case of polyethylene melts examined.[8] It was apparent that the method was able to probe sufficiently low frequencies to reveal tube renewal effects directly. The prediction that the reptational tube renewal time τ_R varies with molar mass as M^3 was consistent with the data. Furthermore the experiment suggested the surprising result that the semilocal motion was molar mass independent whereas the unmodified reptation model suggests that it should vary as M. Despite the common local molecular environment for all hydrogen spins in polyethylene, single exponential proton relaxation was not observed at the low end of the frequency spectrum, despite the fact that BPP relaxation conditions applied. It was therefore apparent in the polyethylene experiment that the chain motion was not common to all regions of the polymer. In particular it appeared that the ends of the chain experienced isotropic rotational freedom and so showed no low-frequency spectral features.

In the present work we extend this study to another polymer melt, poly(ethylene oxide), where the proton relaxation is also associated with the rotation of methylene CH_2 groups. The rotating frame relaxation measure-

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