Identification of Rates and Amplitudes of Macromolecular Motions in *cis*-1,4-Polybutadiene with Coherent Averaging Methods[†]

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ABSTRACT: Coherent averaging techniques are used to identify the nature of the motional process responsible for the residual line width in NMR spectra of *cis*-1,4-polybutadiene. The macromolecular motion is shown to be either a dynamically entangled network or a uniform population undergoing temporally and spatially anisotropic motion. Residual static dipolar interactions account for ~85% of the observed line width in the conventional ^{1}H NMR spectrum and are identified via multiple-pulse, magic angle spinning, and variable-field experiments. Conventional ^{13}C NMR spectra show residual static dipolar and chemical shift contributions to their line width. The contributions of the rate and amplitude of motion to the line width or relaxation time are described by a simple formalism.

Introduction

The investigation of bulk macromolecular motion with solid-state NMR spectroscopy has been a field of interest for more than 20 years[1] and has undergone a renaissance with the advent of modern solid-state NMR techniques.[2] From a very early stage,[1a] the unique importance of the *rate* of the motion has been excessively emphasized for the interpretation of NMR phenomena; the potential importance of the amplitude of the motion was recognized[3] but largely ignored. Only lately[4,5] has it been found that the angular *amplitude* of the motion does indeed play an equally important role for many macromolecules. There are two limiting cases: (1) the motion is effectively spatially isotropic and only the rate(s) of motion(s) are reflected in various NMR parameters (line width, T_1, T_2, $T_{1\rho}$, etc.), and (2) the motion is very rapid on the time scale of the particular NMR experiment and the amplitude of the anisotropic motion primarily determines the NMR parameters. The most common situation for macromolecules is an intermediate case where both the *rate and amplitude* of motion determine the NMR observables. (In the "slow-motion" limit of either very slow motion with a significant degree of spatial averaging or very rapid motion with virtually no degree of spatial averaging, there are no observable effects.)

We demonstrate that modern solid-state NMR techniques employing coherent averaging methods[6] can be used to ascertain the relative contributions of the rate and the spatial amplitude of the motion to relaxation. The use of coherent averaging techniques to make this distinction has been discussed and obliquely demonstrated previously,[4,7,12] although not always appreciated.[8] We present here not only a direct demonstration of the application of coherent averaging techniques to the elucidation of the contribution of spatially anisotropic motion to relaxation but also a formalism for framing the relative contributions of the rate and amplitude of motion to relaxation.

cis-1,4-Polybutadiene has been the subject of many previous investigations. Previous ^{1}H NMR work[4,7,9-14] has demonstrated that the motions extant in this system at or near room temperature are best modeled by a combination of two main modes, one of which is quite rapid ($\tau \sim 10^{-10}$ s) and nearly spatially isotropic and the other of which is quite slow and presumably accounts for the remainder of the spatial averaging. Proton NMR sample spinning (orthogonal to the static magnetic field) experiments[4,7] have shown that at least some small part (~20%) of the residual line broadening is due to static dipolar interactions, and magic angle spinning experiments[12] have shown line narrowing by a factor of 30. ^{13}C NMR investigations[15,16] have subsequently corroborated these observations. Our results demonstrate that either spatial or spin coherent averaging techniques appropriate to either ^{1}H or ^{13}C NMR may be used to measure the amount of any residual *static* interaction (dipolar or chemical shift) present. The determination of the relative amounts of dynamic and static interactions is crucial to an understanding of the manner in which the observed relaxation properties relate to the macromolecular dynamics.

Experimental Results

^{1}H and ^{13}C NMR spectra were acquired at static magnetic field strengths of 1.3 and 7.0 T. The low-field spectra were acquired on a homebuilt spectrometer based upon the design of Vaughan[17] which utilizes the eight-pulse cycle.[18] High-field spectra were acquired on a Bruker CXP-300 NMR spectrometer. The *cis*-1,4-polybutadiene was provided by Professor R. Lenk of the University of Geneva; this sample originated as BR11 polybutadiene from Shell Co.[9]

Figure 1 illustrates low-field proton spectra acquired both via conventional ($\pi/2$) and multiple-pulse methods. The conventional spectrum was obtained by coadding ten free induction decays in the time domain followed by Fourier transformation to the frequency domain. The multiple-pulse spectrum was acquired with a cycle time of 50 μs with a calibrated chemical shift scaling factor[18] of 2.04. The chemical shifts determined from these spectra are $\delta = 2.0$[19] and $\delta = 5.4$; the line widths are 250 Hz ($\pi/2$) and 40 Hz (multiple pulse). The relatively narrow lines observed in the conventional spectrum indicate that the residual nuclear spin interactions (dipolar, chemical shift, and indirect dipolar ("scalar")) are small and may be either dynamic or static in nature. The large degree of narrowing achieved in the multiple-pulse spectrum means that the correlation time of the motion responsible for the broadening must be long, e.g., $\tau_c \gg 10^{-4}$ s. Comparison of the line widths in the two spectra indicates that about 85% of the broadening in the conventional spectrum must be due to *static* dipolar interactions (assuming as usual that indirect dipolar interactions may be ignored).

Figure 2 illustrates high-field proton NMR spectra acquired both via conventional nonspinning ($\pi/2$) and magic

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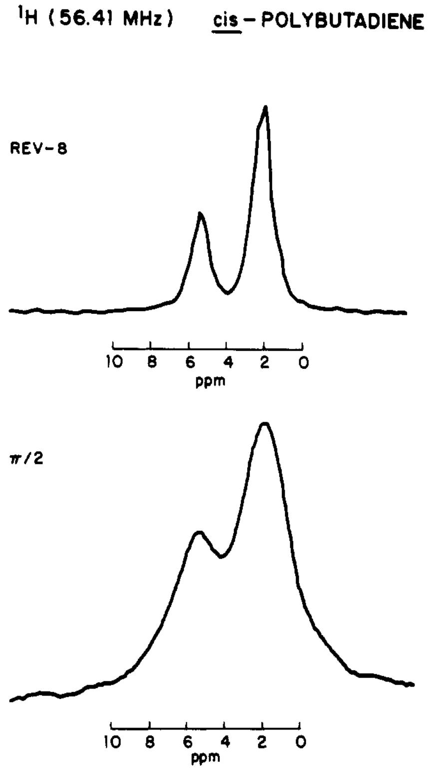

Figure 1. Conventional (lower) and multiple-pulse (upper) proton NMR spectra of *cis*-1,4-polybutadiene acquired at a frequency of 56.41 MHz.

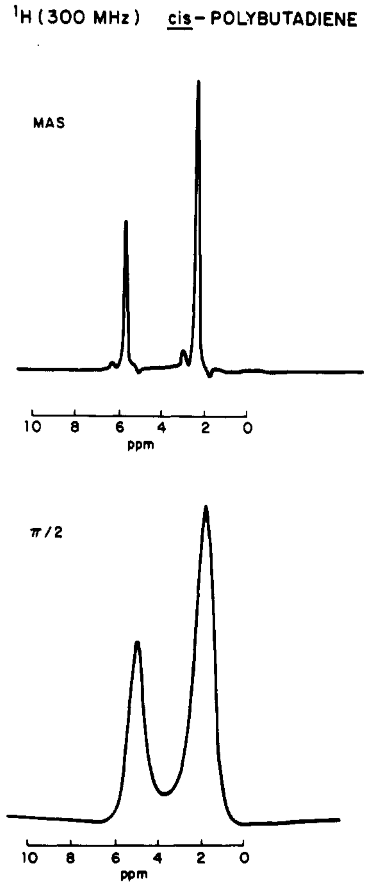

Figure 2. Magic angle spinning (upper) and conventional (lower) proton NMR spectra of *cis*-1,4-polybutadiene acquired at a frequency of 300 MHz.

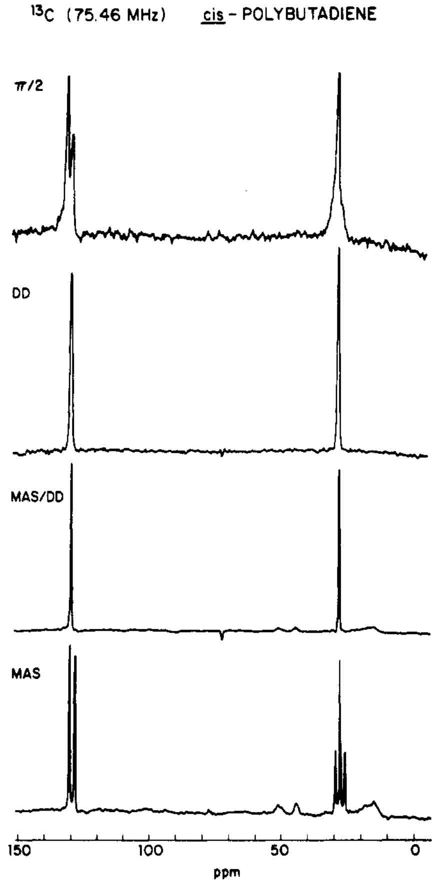

Figure 3. Conventional, proton dipolar decoupled, combined magic angle spinning and proton dipolar decoupled, and magic angle spinning carbon-13 NMR spectra of *cis*-1,4-polybutadiene acquired at a carbon frequency of 75.46 MHz and a proton frequency of 300 MHz.

angle spinning (MAS) methods. The MAS spectrum was obtained in the same manner as the conventional spectrum with the addition of sample rotation at a speed of 3.8 kHz about an axis inclined at an angle of 54.7° with respect to the static magnetic field. The chemical shifts determined from these spectra are $\delta = 2.0$ and $\delta = 5.3$ with respect to external tetramethylsilane and are in good agreement with previous work;[19] the line widths are 260 Hz (static) and 44 Hz (MAS). The large degree of narrowing achieved by magic angle spinning confirms the results obtained from multiple-pulse experiments that the correlation time of interest must be long, $\tau_c \gg 10^{-4}$ s. The observation of the same line width in the conventional spectra at both 1.3 and 7.0 T confirms our previous finding that chemical shift anisotropy contributes a negligible amount to the line width of the ^{1}H spectra. The tenfold increase in resolving power of the MAS spectrum of Figure 2 over that of the multiple-pulse spectrum of Figure 1 is due not only to the larger static magnetic field strength giving rise to larger chemical shift dispersion but also to the fact that the multiple-pulse method gives lower dispersion at constant field due to chemical shift scaling.

Figure 3 illustrates the high-field ^{13}C NMR spectra acquired via conventional methods only ($\pi/2$), with dipolar decoupling (DD) ($\gamma H_1 = 65$ kHz), with combined dipolar decoupling and magic angle spinning at 3.8 kHz (MAS/DD), and with magic angle spinning only (MAS). The chemical shifts and scalar coupling constants obtained from the MAS spectrum are $\delta = 27.4$ and $J = 128$ Hz and $\delta = 129.3$ and $J = 151$ Hz; the chemical shifts are referenced to external glycine (carbonyl $\delta = 176.1$) and agree to within 0.5 ppm of previous solution studies.[19] The fairly narrow lines observed in the conventional spectrum reflect the fact that any residual nuclear spin interactions remaining have been largely averaged and only a small residual broadening remains that could be either dynamic or static. The improved resolution in the dipolar-decoupled spectrum indicates that the majority of the broadening is of a static dipolar nature and the correlation time for the motion is long, $\tau_c \gg 10^{-5}$ s. The improvement in resolution observed with the addition of magic angle spinning indicates that a small part of the residual broadening observed in the conventional ^{13}C spectrum must arise from incompletely averaged chemical shift anisotropy (not from a distribution of isotropic chemical shifts). The good resolution observed in the MAS spectrum indicates that the remaining unaveraged nuclear spin interactions (shown above to be both dipolar and chemical shift in origin) are static in origin and $\tau_c \gg 10^{-4}$ s. The MAS spectrum illustrates the desirability of averaging dipolar interactions with coherent averaging methods (magic angle spinning or multiple-pulse decoupling[27]) that do not also remove scalar coupling information.

Discussion

The salient feature of the spectra of *cis*-1,4-polybutadiene is the narrow resonances ($\simeq$50–250 Hz) that are observed as compared to what is expected for a rigid polymer ($\simeq$10–50 kHz). Narrow lines are observed because the predominant, but not exclusive, motion at room temperature for this elastomer ($T_g \sim -100$ °C) is one involving a *nearly* effectively isotropic reorientation that takes place with $\tau \simeq 10^{-10}$ s[20] which averages $\simeq$99% of the total dipolar and chemical shift interaction. The second mode of motion is one that is characterized by long relaxation times, $\tau_c \sim 0.01$ s,[21] and is responsible for the remainder of the spatial averaging. These two components have been attributed[7] to (1) segmental motions of unentangled chain segments that occur very rapidly and are effectively isotropic and (2) chain entanglements which are spatially and temporally hindered. If this model is correct, we must require either efficacious spin diffusion to homogenize the two nuclear populations in a model with stationary populations or chemical exchange between the two populations in a dynamic entanglement model. The time scale of the mixing process in either model must be much longer than the time scale of the coherent averaging method to allow the coherent averaging process to be effective. A third model is one in which the model of motion does not require a bimodal population but postulates that the motion of the entire chain may be described by two elements, one that is spatially anisotropic and rapid and a second that is essentially static on the time scale of the NMR experiment and accounts for the remainder of the spatial averaging. These two elements have been postulated[12] to be segmental motion and interchain motion (characterized by $\tau_c \sim 10^{-3}$ s), respectively.

We may discriminate between the two bimodal population models by the following considerations. The predominant population is one in which the motion is effectively isotropic and rapid on the NMR time scale and represents $\simeq$99% of the total population (see below). The second population is essentially static and represents $\simeq$1% of the population. The conventional proton NMR spectrum of such a system would appear to be that of a homogeneous system because of either rapid spin diffusion or chemical exchange; a coherent averaging method that is rapid compared to the rate of an equilibration mechanism will yield the observed line narrowing. The observed proton NMR line width of 250 Hz is approximately 1% of the expected static proton NMR line width and arises from a population weighted averaged of the static line width and the line width ($\sim$10 Hz) from the population in the rapid exchange limit. The conventional ^{13}C NMR spectrum of such a system would be that of an apparently homogeneous system for rapid chemical exchange but would appear as a two-component line shape for the spin diffusion mechanism due to the inability of this mechanism to homogenize the populations because of the very slow rate of this process at natural isotopic abundance. Thus, coherent averaging methods have no effect on the ^{13}C line shape of the model where spin diffusion is the equilibration mechanism but will cause the observed narrowing if chemical exchange is the mechanism. Therefore, we are able to rule out the bimodal population model which uses spin diffusion as the equilibration mechanism, and conclude that if the population is indeed bimodal, the two sites must chemically exchange at an exchange rate that would presumably be the rate of chain reptation and represent a dynamically entangled network.

The third model utilizes a uniform population that has dual modes of motion (see above) and may be described by an extension of the method given by Vega and Vaughan.[22] This method has the advantage of explicitly separating the rates and amplitudes of motion in the model. Dipolar relaxation due to the rapid component of the motion may be described in terms of that fraction (ΔM_2) of the total second moment (M_2) which is modulated by the motion. We then have[22]

$$\Delta M_2 = M_2 - M_2^{(0)} \tag{1}$$

In this expression $M_2^{(0)}$ is the effectively static part of the second moment. However, since spatial averaging varies with temperature, the amplitude of this component of the motion will also vary with temperature and we have[23]

$$\Delta M_2(T) = M_2 - M_2^{(0)}(T) \tag{2}$$

The contribution to the relaxation rate (R) is then just

$$R = \Delta M_2(T) f(\tau) \tag{3}$$

where $f(\tau)$ is a spectral density function describing the *rate* of the molecular dynamics and is also temperature dependent. The NMR relaxation behavior will be dominated by the rapid mode of motion, which averages >99% of the appropriate second moment for either proton or carbon-13 NMR. The dipolar contribution to the line shape predicted by this model is represented by that part of the second moment ($M_2(0)$) which corresponds to the static mode. Thus, the line shapes observed in either the ^{13}C or ^{1}H conventional NMR experiments may be substantially narrowed by coherent averaging techniques that are rapid compared to the residual static interaction. Our experimental observations are also in accord with this model, which may be viewed as a uniform population undergoing a motion that is both temporally and spatially anisotropic. Contributions to the line width from residual chemical shift anisotropy, as observed in the ^{13}C NMR spectra, can be framed in the same formalism as the dipolar contribution.

It has been previously shown for *cis*-1,4-polybutadiene that the temperature dependence of the proton line width can be described in terms of the *rate* of motion and the *free volume*.[7] The free volume is related directly to the amplitude of these motions. The present work indicates that two models of motion are possible: (1) an entangled chain with a bimodal population composed of a majority of sites having rapidly, effectively isotropically, reorienting chain segments between entanglement loci and a minority population of static entanglement loci (these two sites exchange individual monomer units by chemical exchange) and (2) a chain described by a single population that has one mode of motion that is rapid and almost effectively isotropic and a second model of motion that is essentially static and accounts for the remainder of the spatial averaging. These two models could be distinguished in a coherent averaging experiment if we were able to distinguish two limiting cases: (a) a bimodal population could give rise to a spectrum consisting of ~99% of the total intensity in a very narrow line and ~1% of the total intensity in a very broad line, and (b) a uniform population would give rise to a spectrum consisting of 100% of the total intensity on a very narrow line. Differentiation of these two possibilities would require a detection linearity and dynamic range greater than 10^6, which is beyond the capabilities of our present instrumentation. A third model, similar to the first, but invoking spin diffusion as the exchange mechanism, is excluded. The compound effects of the rate and amplitude of motion as observed here in proton and carbon-13 NMR experiments have been previously observed in NMR studies of other solid polymers such as poly(tetrafluoroethylene) and its copolymers,[5] poly(methyl methacrylate),[24] polyethylene,[25] and polystyrene.[26] The importance of recognizing the temperature dependence of both the amplitudes and rates of motions, which are both reflected in NMR line width and relaxation data, cannot be underestimated.

Note Added in Proof: Recent results for slow coherent averaging experiments and recently published results for the characteristic time of chain diffusion indicate that only the model of anisotropic segmental motion is reasonable (manuscript in preparation).

Acknowledgment. C.R.D. acknowledges a grant of the National Science Foundation (DMR-8005136) which allowed purchase of parts of the low-field NMR spectrometer used in these studies.

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^{13}C-NMR Relaxation of Polysaccharides: Dextran and Amylose in Dimethyl Sulfoxide and Water

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Received June 28, 1983

ABSTRACT: ^{13}C-NMR spin–lattice relaxation times and nuclear Overhauser enhancements are reported for dextran and amylose in dimethyl-d_6 sulfoxide and D_2O over the temperature range 40–105 °C at 15 MHz. The α-D(1,6)-glycosidic rings of dextran are found to move somewhat more rapidly than the α-D(1,4)-glycosidic rings of amylose in both solvents, and both are somewhat more mobile in water than in dimethyl-d_6 sulfoxide. The derived energy barriers to segmental motions of dextran in both solvents and of amylose in Me_2SO-d_6 are 23 ± 4 and 16 ± 3 kJ/mol, respectively. These figures are slightly higher than those for typical linear-chain molecules.

Introduction

Motional studies of dissolved polymer chains by means of ^{13}C-NMR spin–lattice relaxation time (T_1) and nuclear Overhauser enhancements (NOE) have become significant in addition to other dynamical techniques such as dielectric relaxation, electron spin resonance, and fluorescence depolarization. The method can be applied to almost all polymer solutions, while the other experiments require special labels such as polar groups, free radicals, or fluorescent groups.

Conformational studies[1-3] and solution properties[4,5] of dextran, amylose, and other polysaccharides are described

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0024-9297/84/2217-0449$01.50/0