than reaction with monomeric MMA or STY.

There are significant differences between the chemical shifts for the signals due to benzoate end groups in homopolymers of STY and MMA prepared by using ^{13}C-BPO; in copolymers of these monomers, however, the ester end groups give a single unresolved peak at the intermediate position of δ 166.1.[7] It is not possible therefore to apply the procedure involving NMR examination of end groups for comparison of the reactivities of MMA and STY toward the benzoyloxy radical; this failure can be contrasted with the success achieved with the MMA/STL and STY/STL systems but it can be explained.

For the MMA/STY copolymers, the signals due to the C_6H_5COO(STY)– and C_6H_5COO(MMA)– end groups must be influenced by the distribution of the two types of monomer unit in the attached macromolecular chains and also by steric relationships between the monomer units. In the systems involving STL, the situation is much simpler; in the case of MMA/STL, for example, both C_6H_5COO(STL)– and C_6H_5COO(MMA)– end groups are attached to long sequences of MMA units so that the effects of the units attached directly to the initiator fragment have a dominant effect upon the carbonyl resonances. It should be noted that the NMR spectra referred to here were recorded on a spectrometer operating at 25.05 MHz. Use of a spectrometer operating at higher field has shown that the peak at δ 166.1 for benzoate end groups in the copolymers of MMA and STY consists of several components and that it may be possible to deduce a great deal of information about the relative numbers of the various possible sequences of monomer units in the chains attached to the benzoate end groups.[8]

Polymerizations of MMA in the presence of STL have also been initiated at 60 °C with ^{13}C-AIBN and at 100 °C with ^{13}C-AZOF so that the $(^{13}CH_3)_2C(CN)$– end groups could be studied by NMR spectroscopy. The presence of STL in the systems, even at a concentration sufficient to make [STL]/[MMA] equal to 1.5, has no effect upon the NMR spectra of the polymers. It is evident that STL is not incorporated to any appreciable extent either in the polymer molecule as a whole or at sites adjacent to 2-cyano-2-propyl end groups. It must be concluded that STL is very unreactive toward the $(CH_3)_2C(CN)\cdot$ radical, although it has such high reactivity toward the $C_6H_5COO\cdot$ radical.

The results of studies with other monomers, including acenaphthylene,[7] suggest that high reactivity toward the benzoyloxy radical coincides with comparatively high reactivity toward the 2-cyano-2-propyl radical. In this respect, *trans*-STL is clearly abnormal. Its low reactivity toward carbon-centered radicals, polystyrene and poly(methyl methacrylate) as well as 2-cyano-2-propyl, may result from steric effects which do not operate for an oxygen-centered radical such as benzoyloxy. It will be necessary to test this hypothesis using radicals of other types.

Registry No. STL, 103-30-0; MMA, 80-62-6; STY, 100-42-5; AIBN, 78-67-1; AZOF, 10288-28-5; BPO, 94-36-0.

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Solid-State NMR Investigation of the Contribution of Anisotropic Segmental Motion to Chain Dynamics in *cis*-1,4-Polybutadiene[†]

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ABSTRACT: Solid-state NMR coherent averaging methods and variable-field experiments are combined to illustrate the contribution of anisotropic segmental motion to the chain dynamics of *cis*-1,4-polybutadiene at 25 °C. The macromolecular motion as observed by NMR is shown to be best modeled as rapid anisotropic segmental motion that is spatially inhibited by chain constraints. The lifetime and spatial distributions of these constraints are not reflected in either conventional or coherent averaging NMR experiments for high molecular weight ($\bar{M}_w \sim 3.5 \times 10^5$) *cis*-1,4-polybutadiene.

Introduction

Solid-state NMR spectroscopy has been a valuable method for the characterization of macromolecular dynamics for many years.[1] The application of NMR coherent averaging methods[2] to probe chain dynamics has led to a renewed emphasis on describing the dynamic processes in terms of *both* the rate and angular amplitude of motion.[3-6]

cis-1,4-Polybutadiene has been the subject of many previous investigations. In our initial contribution in this area,[7] we briefly reviewed the previous ^{1}H[4,8-15] and ^{13}C[16,17] NMR results. These investigations have not produced a self-consistent model of the motion, and there is some controversy as to the relative importance of entanglements in interpreting the NMR results. Models have been proposed that attribute the residual line broadening apparent in both the ^{13}C and ^{1}H conventional NMR spectra and/or the spin–lattice relaxation behavior to (1) incomplete motional narrowing arising from insufficiently fast, spatially isotropic motion, (2) spin diffusion between rapidly isotropically reorienting chain segments between entanglements and the entanglements which are temporally and spatially hindered,[14] and (3) anisotropic segmental motion arising from spatial restrictions imposed by entangle-

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[†] Contribution No. 3500.

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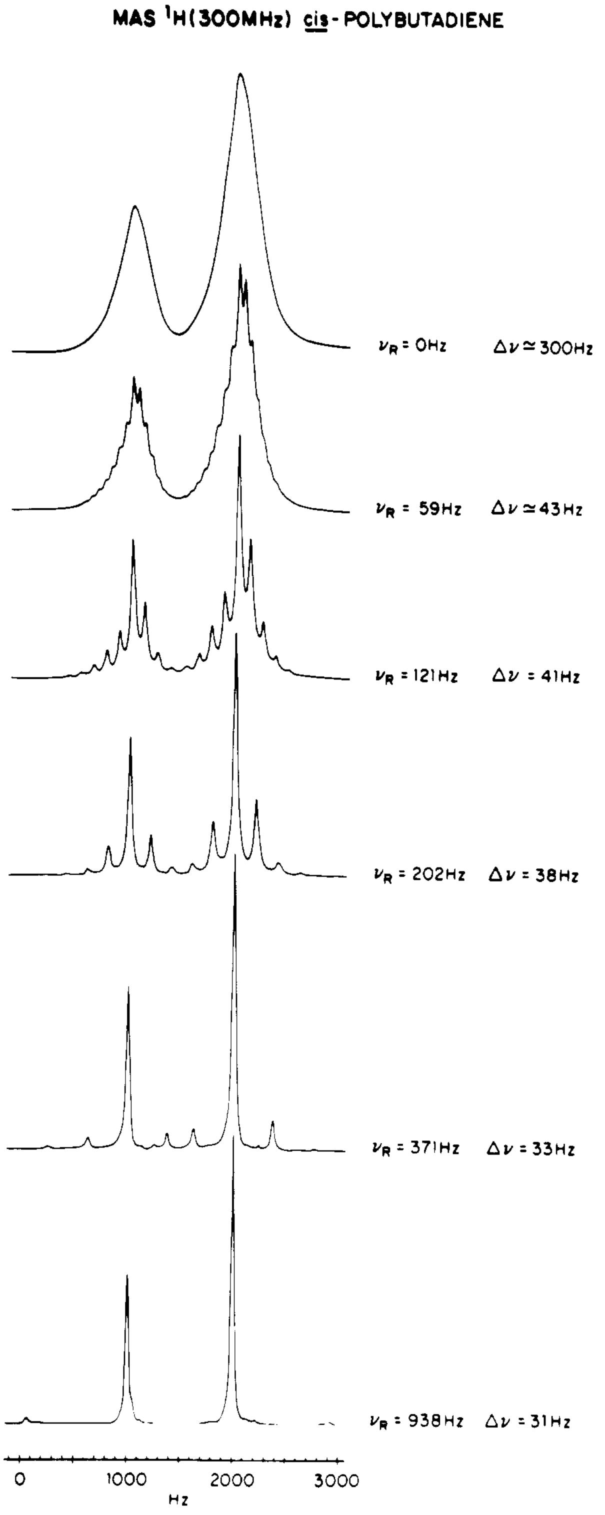

Figure 1. Magic-angle-spinning proton NMR spectra of *cis*-1,4-polybutadiene acquired at a frequency of 300 MHz as a function of spinning rate ν_R.

ments.[17-19] Recent results[20] for *trans*-polybutadiene have shown that microscopic magnetic susceptibility variations are the major factor in producing residual line broadening. We illustrate that the validity of each model may be examined by a combination of NMR coherent averaging methods and variable-field experiments.

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 home-built spectrometer based upon the design of Vaughan.[21] High-field spectra were acquired on a Bruker CXP-300 NMR spectrometer; variable-temperature, low-speed magic-angle-spinning ^{1}H NMR spectra were obtained on a Doty Scientific double-resonance probe which uses a cylindrical rotor supported and driven by a double gas bearing stator. The *cis*-1,4-polybutadiene originated from the Shell Co.[6]

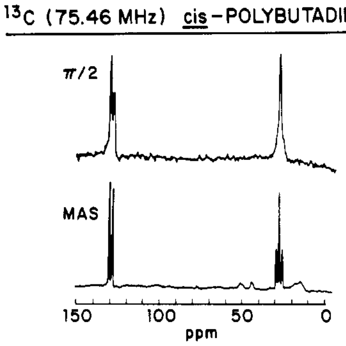

Figure 2. Conventional and magic-angle-spinning carbon NMR spectra of *cis*-1,4-polybutadiene acquired at a carbon frequency of 75.46 MHz.

Figure 1 illustrates ^{1}H NMR spectra obtained at 300 MHz with magic angle spinning at various rates. The spectra were acquired by coadding 32 free-induction decays and then Fourier transforming. These results indicate that the line shape obtained without spinning is inhomogeneously broadened ($\Delta\nu$ = 260 Hz) and the homogeneous broadening inferred from the magic-angle-spinning spectrum is quite small (35 ± 5 Hz) and independent of spinning speed from 60 Hz to 1 kHz. Figure 2 illustrates ^{13}C NMR spectra obtained with and without magic angle spinning (3.8 kHz). Both spectra were acquired without proton decoupling. The residual line width in the MAS spectrum is 15 ± 5 Hz. Chemical shifts and coupling constants for both the ^{1}H and ^{13}C NMR spectra have been previously reported.[7]

Discussion

cis-1,4-Polybutadiene is a highly mobile elastomer ($T_g \sim -100$ °C) at room temperature and, contrary to previous assertions,[22] the dynamic behavior of this system, as reflected by NMR, is most properly discussed in the context of solid-state NMR. The experimental ^{1}H NMR results available from this work and our previous results[7] may be summarized as follows: (1) the line widths are independent of magnetic field strength from 1.4 to 7 T; (2) the line widths are narrowed from 250 to 40 Hz with multiple-pulse averaging (50-μs eight-pulse cycle time); (3) rapid magic-angle-spinning (3.8 kHz) narrows the lines to a width of ~30 Hz; (4) slow magic angle spinning produces a manifold of spinning sidebands for each magnetically distinct proton and the line width of each sideband is essentially independent of spinning speed and is ~30–40 Hz. The ^{13}C NMR results may be summarized as follows: (1) ^{1}H dipolar decoupling removes nearly all of the residual broadening that is observed in a single-resonance spectrum; (2) with both ^{1}H dipolar decoupling and rapid magic angle spinning, further narrowing is observed; (3) the application of rapid magic angle spinning alone yields as much narrowing as when combined with dipolar decoupling.

Proposed Models of Motion. A number of different mechanisms may be considered as causing the residual broadening observed in both ^{1}H and ^{13}C NMR spectra that were acquired in a conventional manner. The first model (quasi-rapid isotropic motion) considers the motion of all chain segments to be isotropic and rapid; however, the rate of the motion is postulated to be insufficiently fast (quasi-rapid) to completely average all dipolar and chemical

Table I
Experimental Results and Predicted Line Narrowing for ^{1}H and ^{13}C NMR Coherent Averaging Experiments for Various Chain Dynamics Models[a]

	^{1}H NMR				^{13}C NMR		
model	REV-8	MAS	slow MAS	decrease H_0	DD	DD/MAS	MAS
quasi-rapid isotropic motion	no	no	no	no	no	no	no
spin diffusion	yes	yes	no	no	no	no	no
chemical exchange							
(1) both sites homogeneously broadened	yes	no	no	no	partial	yes	no
(2) minor site inhomogeneously broadened	no	no	no	no	no	no	no
anisotropic motion							
(1) homogeneously broadened	yes	yes	no	no	yes	yes	yes
(2) inhomogeneously broadened	yes	yes	SSB	no	yes	yes	yes
magnetic susceptibility broadening	no	yes	SSB	yes	no	yes	yes
cis-1,4-polybutadiene experimental	yes	yes	SSB	no	yes	yes	yes

[a] Table entries refer to whether substantial narrowing is expected for each mechanism or is experimentally observed.

shift interactions. In this case, the line shape would be homogeneously broadened. The second model (spin diffusion) postulates that the spin population consists of two types: the vast majority ($\sim$99%) are located between entanglement sites on polymer segments that undergo rapid isotropic motion; the minority are located at entanglement sites, and their motion is both temporally and spatially hindered. The two sites, when protons are the spin of interest, are connected via spin diffusion which produces a homogeneously broadened line whose width ($\sim$500 Hz) is the population weighted average of the line shapes that would be observed for each site in the absence of spin diffusion (e.g., $\sim$10 Hz and $\sim$50 kHz, respectively). The sites are only very weakly coupled when ^{13}C are the spins of interest due to very poor ^{13}C–^{13}C spin diffusion, and the observed line shapes should be a superposition of the line shapes for each site (e.g., $\sim$10 Hz and $\sim$10 kHz, respectively). The third model (chemical exchange) considers the same population distribution as the second model, but here the equilibration mechanism is chemical exchange between the sites ($\tau_e \lesssim 10^{-3}$ s). This model produces a homogeneously broadened ^{1}H NMR line shape whose width is the same as that predicted for the spin-diffusion model if both sites have homogeneously broadened lines, in the absence of chemical exchange. The ^{13}C line shape would be a population weighted average of the line shapes for each site, giving a line of $\sim$100-Hz width.

The fourth model (anisotropic motion) differs from the second and third models in that the motion of all spins on the chain is postulated to be the same, but the motion (rather than the population) has two components. The motion is composed of a rapid component ($\tau_c \lesssim 10^{-10}$ s) whose slight spatial anisotropy leaves a residual broadening ($\sim$1% of a rigid chain) and a very slow component ($\tau_s \lesssim 10^{-3}$ s) that accounts for the remainder of the spatial averaging. This model predicts that the ^{1}H and ^{13}C line shapes would have a width of $\sim$500 and $\sim$100 Hz, respectively, and could be either homogeneously or inhomogeneously broadened, depending upon the rate of the slow motion.

The fifth model (magnetic susceptibility broadening) considers all parts of the chain to undergo rapid isotropic motion, and the NMR line width is determined by microscopic magnetic susceptibility variations within the polymer. This model predicts an inhomogeneously broadened line shape whose width is proportional to magnetic field strength.

Evaluation of Models. The validity of each model may be evaluated by a comparison of the experimental results obtained from the variable-field and six coherent averaging experiments to the results that would be expected for each model. This comparison is summarized in Table I. The quasi-rapid isotropic motion model is eliminated because the time scale of the coherent averaging experiments is too long[2] ($\tau \gtrsim 10^{-2}$–10^{-5} s), compared to an upper bound for the correlation time deduced from the line width observed in the conventional spectrum ($\tau_c \lesssim 10^{-7}$ s), to effect any line narrowing. Line broadening due to magnetic susceptibility broadening can be ruled out because the proton line width is independent of magnetic field strength and the ^{1}H and ^{13}C line shapes are narrowed by proton homonuclear and heteronuclear dipolar decoupling, respectively. The spin-diffusion equilibration model cannot account for the line narrowing observed in the ^{13}C experiments and is thus excluded. If chemical exchange were the proper model, rapid magic angle spinning would still be too slow to have an effect on the line shape of the spins in entangled regions or the spins located on chain segments between entanglements; thus, this model conflicts with the experimental results. The model of anisotropic chain motion resulting in a homogeneously broadened line can be excluded because magic angle spinning much slower than the line width would not produce a manifold of spinning sidebands. The model of anisotropic chain motion which gives an inhomogeneously broadened line behaves in the same manner for each experiment as is observed (Table I).

Thus, the only model that is consistent with all of the experimental data is the one in which very rapid ($\tau_c \lesssim 10^{-10}$ s), slightly spatially anisotropic chain segmental motion averages nearly all nuclear spin interactions to give the narrow line shapes observed at room temperature with conventional methods. In the conventional spectrum, a resonance for each type of proton is observed because the isotropic chemical shift is larger than the residual dipolar broadening. For this reason, each resonance is inhomogeneously broadened because the spin flip-flop term in the nuclear spin dipolar Hamiltonian is no longer effective (to first order). The anisotropy of the segmental motion must be due to constraints that limit the range of orientational fluctuations. The lifetime of these constraints might be thought to be reflected by the residual broadening observed in the coherent averaging experiments.

Residual broadening is observed in all of the coherent averaging experiments: ^{1}H MAS (35 ± 5 Hz), ^{1}H multiple pluse (40 Hz), and ^{13}C MAS (15 ± 5 Hz). The ^{1}H MAS residual line width is approximately a factor of 50 larger than that expected from the lifetime broadening ($T_1 = 0.5$ s). The possibility that the residual broadening reflects some other mode of motion may be probed by examining the temperature dependence of the ^{1}H magic-angle-spinning spectra. Figure 3 illustrates that the residual

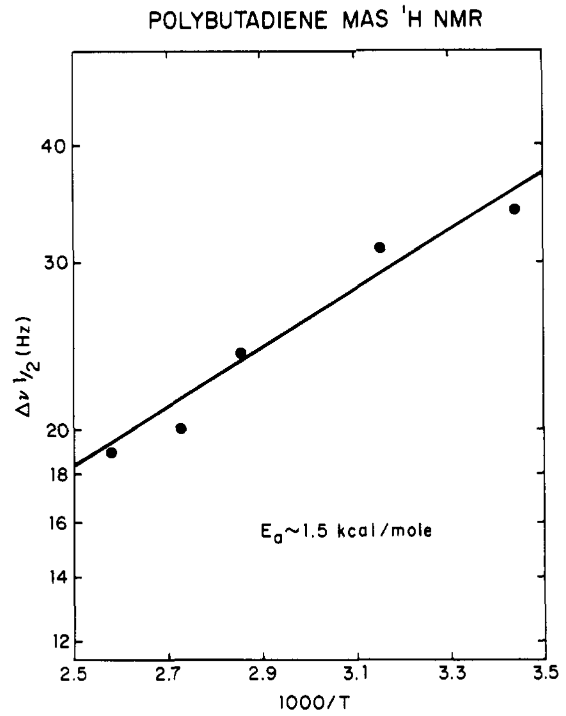

Figure 3. Temperature dependence of the ^{1}H magic-angle-spinning line width for *cis*-1,4-polybutadiene.

broadening decreases with increasing temperature and the apparent activation energy associated with this process is ~1.5 kcal/mol. The residual broadening might be thought to reflect the lifetime of a very slow motion[23,24] such as chain diffusion. This possibility can be excluded because (1) the temperature dependence indicates that the spin system is in the rapid-exchange limit and in this regime the residual broadening should be inversely proportional to the square of the spinning rate,[24] (2) Figure 1 illustrates that the residual broadening in this system is independent of spinning rate, and (3) the activation energy observed is much too small to be consistent with chain diffusion (polypropylene, 10.7 kcal/mol;[25] poly(methyl methacrylate), 13.2 kcal/mol;[26] polyisoprene, 8.7 kcal/mol;[26] polyethylene, 6.7 kcal/mol[27]). The most likely sources of the residual broadening are small static field inhomogeneities, a macroscopic distribution of molecular environments, and the inability of magic angle spinning to completely suppress (to all orders) higher order terms in the spin Hamiltonian; the residual homogeneous dipolar broadening in the nonspinning ^{1}H NMR spectrum is expected to be ~10 Hz. All of these sources of broadening will be averaged to some degree by an increase in the amplitude of motion—thus the observed narrowing of the residual broadening with increasing temperature.

The solid-state NMR experiments presented here demonstrate that the origin of the broadening (260 Hz, ^{1}H NMR) observed in conventional NMR experiments is due to residual static dipolar interactions[28] that reflect a rapid, slightly anisotropic, segmental motion ($\tau_c \sim 10^{-10}$ s) whose anisotropy arises from chain constraints which hindered the degree of spatial averaging. The residual broadening (30 ± 5 Hz, ^{1}H NMR) observed in the coherent averaging experiments does not reflect rates of macromolecular diffusion. These results, for *cis*-1,4-polybutadiene of[29] $\bar{M}_w \sim 3.5 \times 10^5$ at room temperature, indicate that coherent averaging as well as conventional NMR experiments[18] do not reveal any quantitative information about either the very long lifetime (τ_D) of the chain constraints (entanglements) or the characteristic length between an entanglement, unless the time scale of the NMR experiment is much longer than 0.01 s. The experiments define a lower limit for the lifetime of chain constraints: $\tau_D > 0.01$ s.

Acknowledgment. Professor C. R. Dybowski provided the low-field conventional and multiple-pulse ^{1}H NMR spectra. Fruitful discussions with Dr. A. J. Vega and Dr. R. D. Farlee are also acknowledged.

Registry No. Polybutadiene (homopolymer), 9003-17-2.

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