Differential Line Broadening in Coupled Carbon-13 Magic-Angle Sample-Spinning Nuclear Magnetic Resonance Spectra of Solid Polymers[†]

Eric Oldfield,* John Chung, Hong-biao Le, Timothy Bowers, and Jessica Patterson

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801

Gary L. Turner

Spectral Data Services, Inc., 818 Pioneer, Champaign, Illinois 61820 Received November 26, 1991

ABSTRACT: We have observed large differential line broadening (DLB) of the individual components of ${}^{13}C^{-1}H$ coupled multiplets in ${}^{13}C$ "magic-angle" sample spinning (MAS) nuclear magnetic resonance (NMR) spectra of solid poly(*cis*-butadiene), poly(*cis*-isoprene), poly(*cis*,*trans*-butadiene), butadiene–styrene and acrylonitrile–butadiene–styrene block polymers, and poly(*trans*-isoprene). Differential line broadening of olefinic methine carbons is manifest as broadening of the high-field doublet component in poly(*cis*-butadiene) and poly(*cis*-isoprene), while in trans segments in poly(*cis*,*trans*-butadiene) and in poly(*trans*-isoprene) the low-field component broadens first, on cooling. DLB effects for isolated vinyl segments (due to 1,2-addition) in polybutadienes are more pronounced than those seen in the polybutadiene backbone and suggest restricted motion of the vinyl substituent. Results with the block copolymers are very similar to those found with poly(*cis*,*trans*-butadiene) and are thought to be due to dipolar and dipolar–chemical shift anisotropy interference effects. Such DLB effects are largest at high magnetic field strengths and decrease with MAS spinning rate, consistent with such interferences. The observation of differential line broadening using proton-coupled ${}^{13}C$ MAS NMR offers a novel approach to investigating molecular motion in highly mobile solids and may be a useful additional structural characterization technique to the more conventional MAS NMR methods.

Introduction

NMR spectroscopy has now been used for a number of years to investigate mobility in various solid materials. including natural rubber.¹ Much more recently, carbon-13 NMR methods, using cross-polarization $(CP)^2$ and magic-angle sample spinning (MAS),^{3,4} have been applied extensively to investigating polymer structure,⁵ and the CP-MAS technique is now a routine tool for studying such materials. In this method, C-H dipolar and J-coupled interactions are removed by intensive proton irradiation during the ¹³C data acquisition period. It is known, however, that considerable information about molecular structure and motion can be deduced by analysis of coupled-spin relaxation,⁶ and such studies of polymers in solution have been published.^{7,8} It has also been reported that there may be large differences in MAS NMR spinningside-band intensities of the individual components of Jcoupled multiplets in systems having large dipolar and chemical shift anisotropy interactions,⁹ and similar interference effects have been studied in a number of diverse systems—e.g., in fluorophosphate glass,¹⁰ and in the case of MeOH adsorbed on a surface.¹¹ In this paper, we show that large differential line-broadening (DLB) effects may be observed in a variety of solid polymers, by using conventional ¹³C MAS NMR methods but without proton decoupling. We present initial results on variable-temperature proton-coupled ¹³C MAS NMR of cis- and transpolybutadienes and -polyisoprenes, as well as of styrenebutadiene and acrylonitrile-butadiene-styrene block copolymers, and show that large DLB effects are seen in all systems. The effects are largest at high magnetic field strengths, decrease with MAS spinning rates, and offer a

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novel way of investigating mobility in solid (elastomeric) polymers, above T_{g} .

Experimental Section

Carbon-13 MAS NMR spectra were obtained on "home-built" Fourier transform NMR spectrometers, which operate at 125, 90, and 68 MHz for ¹³C. These instruments utilize Oxford Instruments (Osney Mead, U.K.) 11.7-T 2-in.-, 8.45-T 3.5-in.-, or 6.3-T 2-in.-bore superconducting solenoid magnets, Nicolet (Madison, WI) Model 1280 computer systems, and a variety of digital and radio-frequency electronics. MAS NMR sample probes were from Doty Scientific (Columbia, SC). Poly(cis-butadiene), poly(cis,trans-butadiene), poly(trans-isoprene), and acrylonitrile-butadiene-styrene resin were from Aldrich (Milwaukee, WI). Poly(cis-isoprene) was from Alliance Rubber Co. (Alliance, OH). The styrene-butadiene copolymer was Dexco (Dow/Exxon, Plaquemine, LA) Vector triblock polymer 6201-D having a triblock styrene-butadiene-styrene structure, with 28.1% styrene and block molecular weights 9200 (styrene) and 47 500 (butadiene), and was provided by B. Walther and M. Meadows.

Chemical shifts are all referenced with respect to an external sample of tetramethylsilane (TMS), with low-field, high-frequency, paramagnetic or deshielded values designated as positive (IUPAC δ scale).

Results and Discussion

By way of introduction to the topic of differential line broadening, we show in Figure 1A the proton-coupled ¹³C MAS NMR spectra of a sample of liquid glycerol, as a function of temperature. As expected, the spectra consist of a CH J-coupled doublet (at ~73 ppm downfield from TMS), and a CH₂ J-coupled triplet (at ~63 ppm). On careful inspection, however, it can be seen from Figure 1A that the peak heights of the individual J-coupled multiplets are distorted from the 1:1 or 1:2:1 ratios expected



Figure 1. 125.7-MHz (11.7-T) proton-coupled ¹³C MAS NMR spectra of glycerol and poly(*cis*-butadiene) as a function of temperature: (A) glycerol; (B) poly(*cis*-butadiene). Experimental conditions were as follows: 3-4-kHz MAS, 40-1332 scans, a 5-s recycle time, $5-7 \mu s$ (90°) pulse widths, and 1-Hz line broadening due to exponential multiplication. Sample temperatures are indicated on the right of the figure.

for a conventional mobile liquid, an effect which is accentuated upon cooling. The reason for this is that, especially at low temperatures, the glycerol molecules undergo slow (and anisotropic) reorientation, and there are complex intereference effects between the inter- and intramolecular dipolar and ¹³C chemical shift anisotropy interactions, which result in different spin-spin and spinlattice relaxation rates for the individual multiplet components.⁶ At low temperatures, glycerol is a glassy material, and the line-broadening effects observed are analogous to those observed by Farrar et al. in a highly viscous sodium fluorophosphate-H₂O glass—where the larger chemical shift anisotropy and dipolar interactions make the differential line-broadening effects even more pronounced.¹⁰

A pictorial view of one of the origins of differential line broadening has been given by Harris et al.,⁹ who showed for an A-X dipolar interaction in a rigid solid that, in the presence of a sizable A-spin chemical shift anisotropy, the components of the Pake doublet may be thought of as being either broadened or narrowed, and, under MAS, two spinning-side-band manifolds—a broad and a narrow one, separated by ${}^{1}J_{AB}$ —could be observed. In the presence of fast overall molecular motion, T_2 relaxation reflects this interference between the two static interactions. The result is that transverse (and longitudinal) relaxation rates of the individual components of J-coupled multiplets may be very different. The actual component line widths, T_1 and T_2 values, are determined by the rates and types of motion, the sign of J, and the magnitudes and orientations of the two (or more) tensors. We have seen such differential



Figure 2. 125.7-MHz (11.7-T) proton-coupled ¹³C MAS NMR spectra of poly(*cis*-isoprene) as a function of temperature. Experimental conditions were as follows: 20 °C, 3.4-kHz MAS, 400 scans; -5 °C, 3-kHz MAS, 900 scans; -15 °C, 3-kHz MAS, 1012 scans; -25 °C, 3.2-kHz MAS, 1024 scans. A 5-s recycle time, 7- μ s (90°) pulse widths, and 1-Hz line broadening due to exponential multiplication were used in each spectrum.

line-broadening effects due to T_2 relaxation in a range of solid, mobile polymers. For example, we show in Figure 1B the 11.7-T ¹³C MAS NMR spectra of a sample of solid poly(cis-butadiene), as a function of temperature. Upon cooling, there is a broadening of all multiplet components, with the effect being largest for the high-field component of the olefinic methine doublet centered at ~ 130 ppm downfield from TMS (Figure 1B). DLB effects for the methylene carbon are much smaller, due in part to its much smaller chemical shift anisotropy. Results with poly-(cis-isoprene) as a function of temperature are shown in Figure 2. In the low-field region of the spectrum (Figure 2A), there is again a major differential broadening of the high-field component of the methine doublet (at ~ 126 ppm), consistent with the result found with the poly(cisbutadiene) (Figure 1B). There is, however, a much larger broadening of both olefinic methine doublet components at lower temperatures in the poly(cis-isoprene) than in the poly(cis-butadiene), due to the considerably lower T_g $(\sim -102 \text{ °C versus } -67 \text{ °C})$ for the polybutadiene. As has been found with other (2H) NMR studies investigating line broadening in polybutadienes,¹² our results are consistent with observations of narrow-line spectra ≈ 40 °C above calorimetrically determined T_{g} temperatures. However, with ²H NMR, the collapse of the ²H quadrupole splittings in elastomers removes the interesting ²H quadrupole tensor information.

Figure 2 also shows DLB effects on each of the CH_2 and CH_3 multiplet components (Figure 2B) basically as observed previously in the case of MeOH adsorbed onto a silica surface.¹¹ While perhaps surprising, similar DLB effects have been observed by us in a number of hydrocarbon groups in polymers and liquid crystals and are not restricted to carbons bound to oxygen, where CSA values are expected to be larger. Spin-spin relaxation measurements (using synchronized excitation sample spinning) at both 11.7 and 6.3 T give moderately good agreement between the experimentally observed widths and $1/\pi T_2$ only below room temperature, due to the increased importance of instrumental broadening and sample heterogeneity/susceptibility effects at the higher temperatures. For example, at 20 °C and 11.7 T, the observed T_2 values for the olefinic methine carbon doublet are 56 and 34 ms ($\pm 20\%$), corresponding to $W = 1/\pi T_2 = 5.7$ and 9.3 Hz, while the experimental widths are ~ 25 and 28 Hz. At -8 °C, however, we find $T_2 = 8.4$ and 5.0 ms, $W = 1/\pi T_2$ = 38 and 64 Hz, and the experimental widths are 44 and 78 Hz.

We have also investigated several polymers containing trans double bonds, which might be expected to display



Figure 3. 125.7-MHz (11.7-T) proton-coupled ¹³C MAS NMR spectra of poly(*cis*,*trans*-butadiene) segments in several polymers: poly(*cis*,*trans*-butadiene) at (A) +22, (B) -20, and (C) -30 °C; (D) a styrene-butadiene block copolymer (Dextrel), -20 °C; (E) acrylonitrile-butadiene-styrene resin, 23 °C. Spectral conditions are all basically as in Figures 2 and 3. The features on the left and right (c and d) are shown with vertical expansions.

somewhat different DLB behavior, due at least in part to the different orientations of the dipolar and shielding tensors with respect to the chain axis and the possibilities of different axes of motional averaging in the cis and trans olefinic segments. Figure 3 shows 11.7-T ¹³C MAS NMR results on a poly(cis,trans-butadiene), as a function of temperature (Figure 3A-C), as well as a similar spectrum of a styrene-butadiene block polymer (Figure 3D), at -20 °C, and an acrylonitrile-butadiene-styrene copolymer, at 23 °C (Figure 3E). There are four main features of interest in Figure 3, which we have labeled a-d. The feature labeled a arises from the *cis*-butadiene carbons (adjacent to either cis or trans residues), while that labeled b arises from the trans olefinic carbons. A full discussion of the large number of peaks observed in polybutadienes is given elsewhere.¹³ Upon cooling, the cis segments (a) undergo differential line broadening, with the high-field component broadening more rapidly than the low-field component, just as was found with the poly(cis-butadiene) and poly(cis-isoprene) (Figures 1 and 2). In contrast, the trans segments (b) show the opposite behavior, with the low-field component broadening more rapidly on cooling than the high-field component. Moreover, the results of spectral simulations (data not shown) confirm the observation that the trans segments broaden overall more rapidly than the cis segments (Figure 3C). Very similar behavior is observed in the aliphatic carbon region, and results in the styrene-butadiene and acrylonitrilebutadiene-styrene block copolymers mirror those seen with the cis, trans-butadiene. These results indicate that

the cis and trans segments in poly(cis,trans-butadiene) and the styrene-butadiene and acrylonitrile-butadienestyrene block copolymers appear to undergo rather different local motions. In both the olefinic and aliphatic carbon spectral regions, the line widths of the trans segments are larger than those of the cis segments, an effect that is accentuated at low temperatures. We believe that the most likely origin of the overall line width, and DLB effects, may originate in the occurrence of different local motions for the cis and trans methine carbons, with presumably a rotation of the cis unit about the C1-C4 axis causing additional narrowing of both the cis olefinic and methylene carbon resonances, as illustrated below by the arrows:



Such a motion would be impossible for a trans segment.

There are two other interesting features in Figure 3, labeled c and d. These peaks arise from vinyl groups produced during 1,2-addition and at room temperature give rise to a doublet (c, \sim 143 ppm) and a triplet (d, \sim 115 ppm). On cooling to -20 °C (Figure 3B), there are very pronounced DLB effects for both the doublet and triplet high-field peaks, and by -30 °C broadening of all transitions is pronounced (Figure 3C) even though the mainchain olefinic carbons remain relatively narrow. The large broadening of the vinyl methylene carbon must arise in part from the enhanced dipolar broadening due to the presence of two, rather than one, protons, although the peak is substantially broader than that of either saturated methylene carbon -30 °C (data not shown). This, combined with the much larger DLB of the vinyl methine versus the main-chain methine resonances, indicates a decreased mobility for the vinyl carbons.

The vinyl segments occur in relatively isolated regions of the 13 C spectrum, and we have been able to confirm the CSA-dipolar origins of their DLB by obtaining coupled MAS NMR spectra as a function of magnetic field strength and as a function of MAS spinning rate. Parts A and B of Figure 4 shows typical MAS spectra for the vinylic carbons in a 72% trans-polybutadiene at 6.35, 8.45, and 11.7 T, all at a 3.00-kHz MAS rate, and Figure 4C shows the effect of MAS rate (from 2 to 10 kHz) on the sp² methylene DLB. The experimental spectra indicate that DLB effects (as measured from peak height ratios) are larger at 11.7 T than 8.45 or 6.35 T and, with increasing MAS rates, become much smaller—consistent with the CSAdipolar mechanism suggested previously.

Finally, since the cis and trans carbons in the polybutadienes (Figure 3) show rather different line-width and DLB effects, we have obtained the coupled ¹³C MAS NMR spectrum of (the amorphous region of) a poly(trans-isoprene) and show this result, together with that of a poly-(cis-isoprene), in Figure 4D. Just as observed with the cis- and trans-butadienes, we find a reversal of the DLB effect for the trans methine carbon from that observed with the *cis*-isoprene sample. The observation that the spin-lattice relaxation rates of the upfield component of the methine doublet in both cis- and trans-polyisoprenes are faster than that of the downfield component¹⁴ while the DLB effects have opposite line broadenings indicates that the signs of the interference terms change, depending on whether high (T_1) or low (T_2, DLB) frequency motions are being sampled. Moreover, the reversed DLB sign in



Figure 4. Proton-coupled ¹³C MAS NMR spectra of polymers showing the effects of magnetic field strength, spinning rate, and cis/trans double bond isomerism on observed differential line broadening in the olefinic carbon region: (A) vinyl methine carbon in polybutadiene (72% trans) at 6.35 (top), 8.45 (middle), and 11.7 T (bottom), 3.00-kHz MAS rate; (B) as in A but for vinyl methylene carbon; (C) same sample as in A but with a MAS rate of 2.00 (top), 6.00 (middle), and 10.00 kHz (bottom), at 11.7 T; (D) poly(cis-isoprene) (top) and poly(trans-isoprene) (bottom). All samples are at 23 °C.

the poly(*trans*-isoprene) implies that the C-H vector must be undergoing fast motion about an axis approximately perpendicular to the C-H bond axis.¹⁴

Conclusions

To date, a limited number of "condensed" systems (viscoelastic micelles, sonicated lipid vesicles, a viscous glass) have been investigated using solution NMR coupled relaxation methods, and there have been two MAS NMR studies, one of MeOH on a silica surface¹¹ and one of the methylene carbon of *cis*-butadiene, at low field⁸—the latter being investigated by longitudinal relaxation. However, all coupled spin systems whose NMR spectra are narrowed considerably on MAS are candidates for DLB-coupled spin relaxation investigation, where in general there are more parameters which can be fitted to models of molecular motion than *with* decoupling. Thus, elastomers above T_g , liquid crystals, and biochemical systems ranging from pulmonary surfactant to atherosclerotic plaque show DLB effects, and in some cases we have found good evidence for C-H vector orientational information similar to that deduced by ²H NMR but without use of ²H labeling.^{14,15} In the cases we have discussed in this paper, our results suggest strong similarities between the poly-(*cis*-butadiene) and poly(*cis*-isoprene) local motions and between *trans* segments in poly(*cis*,*trans*-butadiene) and poly(*trans*-isoprene). Trans segments are less mobile than cis segments, while vinyl groups (produced during 1,2addition) are less mobile than either.

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References and Notes

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