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Chemical Shift-Related Artifacts in NMR Determinations of Proton Residual Dipolar Couplings in Elastomers

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Introduction

Proton transverse NMR relaxation continues to enjoy great popularity for the characterization of rubbers with respect to their cross-link density or their chain dynamics.[1] The target quantity extracted from these as well as other more elaborate experiments[2] is usually the residual second moment, or its square root, the residual dipolar coupling ($D_{\rm res}$), which arises from fast nonisotropic fluctuations of the network chains and is directly proportional to the cross-link density.[3,4]

In particular Hahn echoes represent a deceptively simple approach, which however suffers from sometimes strong model assumptions inherent to the functions used for the interpretation of the data. Only recently, one of us has shown that fits to the widely used Andersen−Weiss model, which yield $D_{\rm res}$ as well as a supposed correlation time of slow cross-link fluctuations, suffer from serious artifacts.[5] These are related to minor changes in the shape of the relaxation curves as a function of filler content or magnetic field strength, which in turn lead to physically meaningless fit results for $D_{\rm res}$ and the slow correlation time. We here demonstrate another important source of error arising at high field, which renders a conclusion of a recent publication on the methine group contribution to the transverse relaxation in natural rubber (NR), as well as some conclusions of other works, incorrect.

Steren et al.[6] have separately analyzed the relaxation of the methine and methylene/methyl magnetizations, which are resolved at high Larmor frequency (a few hundred MHz) in weakly cross-linked NR, and found significantly lower apparent coupling constants for the methine group. This finding is an artifact related to a second averaging of the (weak) homonuclear residual dipolar coupling by the (stronger) chemical shift difference of the coupling partners. This effect arises in all types of experiments which are not compensated for chemical shift differences, and can be circumvented by using either Carr−Purcell−Meiboom−Gill (CPMG) experiments or, more reliably, broad-banded proton multiple-quantum (MQ) spectroscopy.[7]

Results and Discussion

Figure 1a displays typical transverse relaxation data for an NR sample obtained on a 500 MHz spectrometer, on which two spectral components, the methine and methylene/methyl resonances, appear well separated. Most notably, data from relaxation time-incremented Hahn echo experiments suggest weaker residual dipolar couplings for the methine group, as is apparent within the first 8 ms of the intensity decay.

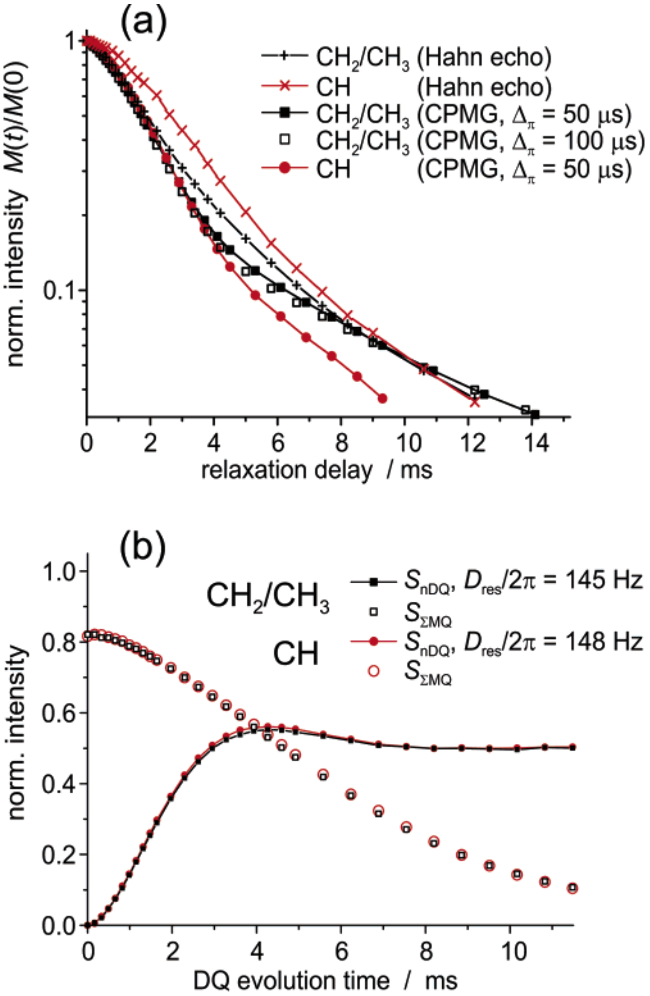

Figure 1. Proton transverse relaxation (a) and MQ data (b) of a natural rubber sample vulcanized with 1 phr sulfur. Data were acquired on a Bruker Avance 500 MHz spectrometer at 80 °C. The DQ build-up data ($S_{n\rm DQ}$) in part b was normalized according to the protocol described in ref 7 after subtraction of a sol/dangling chain component of about 18% from $S_{\Sigma\rm MQ}$.

As shown in our previous note,[5] an expression of the type

$$\frac{M(t)}{M(0)} = A \exp\left\{-\frac{9}{40} D_{\rm res}{}^{2} t^{2}\right\} + B \exp\{-t/T_{\rm 2B}\} \quad (1)$$

should be used to fit such data. B represents the mobile chain fraction, and if necessary, a third component C can be added in order to better represent the long-time tail, which is composed of sol and dangling chains. Importantly, the A part assumes a dephasing of network chain magnetization by a single residual dipolar coupling, and is based on the second-moment approximation.[8,9] Effects such as slow dynamics or distributions of couplings change the shape of the relaxation curves, but as these shape changes are nontrivial and not

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Table 1. Results for D_{res} (in rad/s) in Natural Rubber Obtained by Fitting the Data of Figure 1 to Eqs 1 and 4[a]

	Hahn echo		CPMG $\Delta_\pi = 100\ \mu s$		CPMG $\Delta_\pi = 50\ \mu s$		DQ build-up	
	CH	$CH_{2/3}$	CH	$CH_{2/3}$	CH	$CH_{2/3}$	CH	$CH_{2/3}$
D_{res}	**112**	163	164	183	169	181	148	145

[a] The relaxation time of the 18% sol contribution was about 8−10 ms in all cases.

known a priori, the use of more complex functions based on specific interpretations of a non-Gaussian shape (e.g., Andersen−Weiss approximation plus slow rotational diffusion) leads to incorrect fitting results. Equation 1 does not represent the initial decay well in all cases, but it provides a reliable average over an unknown distribution, with an only weak bias due to slow dynamics when the experiments are conducted sufficiently far above the glass transition.

Results from fits to the data in Figure 1 are listed in Table 1. The Hahn echo data suggest that the residual coupling associated with the CH group is about $^2/_3$ of the average coupling experienced by the $CH_{2,3}$ groups. However, such a comparison is misleading, as the strongest couplings associated with $CH_{2,3}$ are presumably the ones among the constituent protons, while the CH proton is more likely to be coupled to $CH_{2,3}$ rather than to its own kind located roughly one monomer unit length away. Then, the isotropic chemical shift difference has to be taken into account, as the chemical-shift (Zeeman) and homonuclear dipolar Hamiltonians do not commute:[10]

$$[(\omega^i_{CS}\hat{I}^i_z + \omega^j_{CS}\hat{I}^j_z),\omega^{ij}_{Dres}(2\hat{I}^i_z\hat{I}^j_z - \hat{I}^i_+\hat{I}^j_- - \hat{I}^i_-\hat{I}^j_+)] \neq 0 \tag{2}$$

Obviously, $(\omega^j_{CS} - \omega^i_{CS})/2\pi$ for the CH and $CH_{2,3}$ groups is on the order of 3.5 ppm × 500 MHz = 1750 Hz, while $\omega^{ij}_D/2\pi$ is less than 200 Hz. Then, second averaging of the dipolar Hamiltonian by the chemical-shift Hamiltonian can be considered almost complete,[11] and the dipolar Hamiltonian loses the flip-flop terms:

$$\hat{H}^{ij}_{Dhet} \approx \omega^{ij}_{Dres}2\hat{I}^i_z\hat{I}^j_z \tag{3}$$

The inter-group homonuclear coupling therefore takes the form of a *heteronuclear* coupling, the time evolution of which is governed by a coupling constant which is effectively $^2/_3$ weaker ("weak coupling limit").

This second averaging can be suppressed by rapid refocusing of chemical shifts on a time scale shorter than the characteristic dipolar evolution time, $1/\omega^{ij}_{Dres}$, and is for instance realized in a Carr−Purcell−Meiboom−Gill (CPMG) relaxation experiment. We have performed such experiments, where the relaxation delay time was increased by incrementing n according to the pulse sequence $(\pi/2)_x - [(\Delta_\pi/2) - \pi_{(\pm y,\pm y,\mp y,\mp y)} - (\Delta_\pi/2)]_n - acq$. The indicated phase cycling of subsequent π pulses is essential to reduce distortions of the relaxation curves due to pulse imperfections and pulsed spin-lock effects. Acquisition was started the top of the last echo of a train of overall length t, and the FID was Fourier transformed to obtain spectra.

The data in Figure 1a and Table 1 show that the CPMG relaxation decays detected at the CH and $CH_{2,3}$ positions are very similar and not much dependent on the pulse spacing Δ_π. The apparent residual couplings agree within 10%, while in the Hahn echo experiment, they appear to be different by a factor of $^2/_3$, in agreement with the quantum-mechanical prediction. Steren et al. have reported a smaller ratio of about 0.4,[6] which is incorrect due to the use of the critical Andersen−Weiss fitting function. Note that it is not easy to eliminate the influence of experimental imperfections of long CPMG π pulse trains on the transverse magnetization decay, as it is particularly apparent as changes in the shape of the long-time tails. This can also bias the fits to eq 1, and might explain the weak discrepancies.

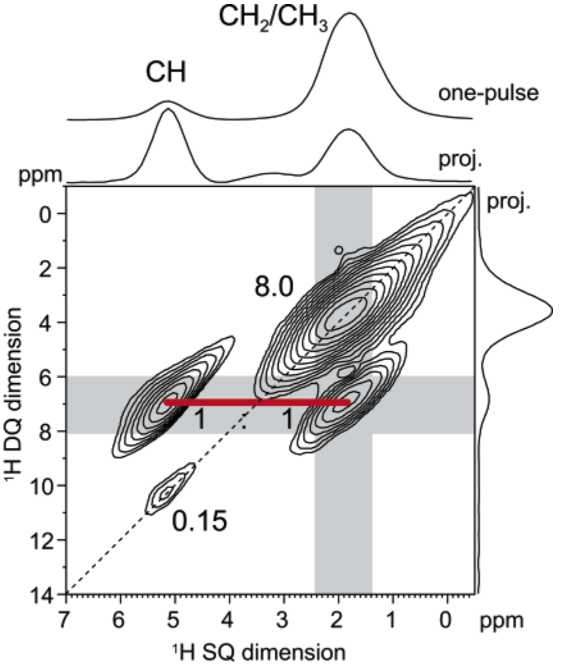

Figure 2. 2D proton DQ correlation spectrum of the natural rubber sample using 8 cycles of 200 μs each of the improved[7] DQ pulse sequence of Baum and Pines[14] for excitation and reconversion. The projections are summed over the gray shaded areas, and the numbers represent the relative peak areas.

As evidenced by our previous work,[5,7,12,13] proton MQ spectroscopy is the more robust choice for investigations of elastomers, provided that a repetitive pulse sequence with a sufficiently short cycle time and a pure average double-quantum (DQ) Hamiltonian is used. Note that this is not the case for some of the published work in this area, in particular for the static two-pulse DQ segment favored by the Aachen group.[2] Field-dependent second-averaging effects can of course also be avoided by conducting the experiments on low-field spectrometers.[5,12]

The DQ build-up curves in Figure 1b obtained with 200 μs-cycles of a compensated DQ pulse sequence[7] give additional evidence that the residual couplings detected at both resonances are very similar. Within the second-moment approximation, the normalized build-up can be fitted to[8,13,15]

$$S_{nDQ} = 0.5\left(1 - \exp\left\{\frac{2}{5}a(\psi)^2 D_{res}{}^2 t_{DQ}{}^2\right\}\right) \tag{4}$$

where t_{DQ} is the length of the DQ excitation or reconversion time, and $a(\psi)$ is a cycle time-dependent scaling factor (0.82 in the present case). The results in Table 1 indicate slightly lower values as compared to relaxometry. As discussed in our previous note,[5] this discrepancy is straightforwardly explained in terms of the different averaging of eqs 1 and 4 over a distribution of couplings. Effects of slow dynamics are further removed by the normalization of the DQ build-up by the MQ sum intensity, $S_{\Sigma MQ}$. The normalized DQ build-up functions are even amenable for distribution analysis,[7] yet this is beyond the present scope. Figure 1b also shows the decays of $S_{\Sigma MQ}$, which indicate that the MQ coherences associated with CH and $CH_{2,3}$ relax as a result of the same (slow) process.

Finally, Figure 2 depicts a two-dimensional DQ correlation spectrum, from which it is immediately obvious that indeed, CH groups are mostly coupled with $CH_{2,3}$ groups (vertical bar), while the signal associated with the latter is dominated by intra-resonance interactions (peak located on the dashed DQ diagonal). When taken at short DQ evolution time (and possibly under magic-angle spinning conditions), the relative signal areas in such spectra can be used to determine the relative size of inter- and intra-group couplings, whereby the local dynamics of the monomer units can be investigated more closely.[16] Earlier attempts to establish monomer-specific models using 2D magnetization exchange spectroscopy in rubbers[17] must also be considered erroneous, due to the neglect of the effects of second averaging.

Conclusions

We have identified yet another serious source of artifact which renders proton Hahn echo as well as other uncompensated experiments aimed at the determination of residual dipolar couplings in rubbers with different functional groups unreliable. Once the chemical-shift separation of dipolar-coupled protons exceeds the residual dipolar couplings, i.e., once the resonance frequency difference starts to exceed the line width and the signals appear separated, second averaging changes the nature of the dipolar coupling Hamiltonian and thus the magnitude of apparent inter-group residual coupling constants. This is a well-known phenomenon, but its importance in elastomer investigations has not yet been appreciated. Ultimately, the resulting field-dependent changes in the shape of the relaxation curves may be one reason for the discrepancies found upon fitting high- and low-field relaxation data to the Andersen−Weiss function.[5]

Rapid shift refocusing in CPMG experiments represents one alternative to suppress this effect, yet at the expense of distortions of the relaxation curves, in particular at longer times. Once again, proton MQ spectroscopy using a robust DQ excitation pulse sequence and a reliable intensity normalization approach represents in our hands the best alternative for quantitative investigations. It compensates for the effects of slow motions and therefore permits even the estimation of distributions of residual couplings. The DQ method is after all robust and easy to set up, and it can also be performed on cost-efficient low-field instrumentation without compromise in data quality.[12]

Several works published in the past few decades, in particular those on butadiene and styrene−butadiene rubbers, will need to be revised in the light of the present finding. Note again that the caveat pertains not only to Hahn echo relaxometry at moderate and high magnetic fields but also to more elaborate experiments such as uncompensated DQ and magnetization exchange experiments under static or magic-angle spinning conditions. The simplicity of Hahn echoes may of course still be taken advantage of when comparisons among rubbers of similar kinds are sought, but without a proper field-dependent calibration, further interpretations of the data in terms of residual couplings, order parameters, or absolute cross-link densities should be avoided.

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