Enhanced sensitivity to residual dipolar couplings of elastomers by higher-order multiple-quantum NMR

R. Fechete,[a,b] D.E. Demco,[a] and B. Blümich[a,*]

[a] *Institut für Technische Chemie und Makromolekulare Chemie, Rheinisch-Westfälische Technische Hochschule, Worringerweg 1, D-52056 Aachen, Germany*
[b] *Technical University Cluj-Napoca, Daicoviciu 1, R-400020 Cluj-Napoca, Romania*

Abstract

The homonuclear and heteronuclear residual dipolar couplings in elastomers reflect changes in the cross-link density, temperature, the uniaxial and biaxial extension or compression as well as the presence of penetrant molecules. It is shown theoretically that for an isolated methyl group the relative changes in the intensity of the homonuclear double-quantum buildup curves in the initial time regime due to variation of the residual dipolar coupling strength is less sensitive than the changes in the triple-quantum filtered NMR signal when considering the same excitation/reconversion time. For a quadrupolar nucleus with spin $I = 2$ the sensitivity enhancement was simulated for four-quantum, triple-quantum, and double-quantum buildup curves. In this case the four-quantum build-up curve shows the highest sensitivity to changes of spin couplings. This enhanced sensitivity to the residual dipolar couplings was tested experimentally by measuring ^{1}H double-quantum, triple-quantum, and four-quantum buildup curves of differently cross-linked natural rubber samples. In the initial excitation/reconversion time regime, where the residual dipolar couplings can be measured model free, the relative changes in the intensity of the four-quantum buildup curves are about five times higher than those of the double-quantum coherences. For the first time proton four-quantum coherences were recorded for cross-linked elastomers.
© 2004 Elsevier Inc. All rights reserved.

Keywords: ^{1}H double-quantum; Triple-quantum; Four-quantum coherences; Residual dipolar couplings; Cross-linked natural rubber

1. Introduction

Homonuclear and heteronuclear residual dipolar or quadrupolar interactions measured by NMR methods represent an important source of information about the structure and molecular dynamics in soft solids like elastomers and biological tissues [1–3]. Using these quantities structure–function relationships can be investigated for the broad class of elastomer materials [2]. The difficulties related to these measurements are due to the small values of the residual spin couplings compared to those of other spin interactions, the many-body character of the dipolar couplings and the presence of molecular motions which produce a supplementary encoding of the spin system response.

One important objective of the NMR spectroscopy applied in the field of elastomers is to develop methods that are accurate and highly sensitive to the changes in the values of the residual dipolar couplings. One-dimensional (1D) NMR methods based on the dipolar correlation effect in combination with Hahn and solid echoes [4,5], the stimulated echo [6], the magic echo [7], and magnetization-exchange [8] provide access only to the second van Vleck moment via a model which takes into account the solid-like and liquid-like contributions to the spin system response [9]. Model free access is given by the analysis of multiple-quantum built-up [10–14] and decay [15] curves recorded in the initial regime of the excitation/reconversion periods as well as the accordion magic sandwich technique [16]. Chemically site selective residual dipolar couplings can be elucidated by two-dimensional (2D) NMR spectroscopy using, for instance, ^{13}C–^{1}H heteronuclear residual dipolar encoded

* Corresponding author. Fax: +49-241-80-22-185.
 E-mail address: bluemich@mc.rwth-aachen.de (B. Blümich).

spinning sideband patterns [17], NOESY under magic angle sample spinning (MAS) [18], and DQ MAS NMR spectroscopy [19].

Multiple-quantum (MQ) coherences show an enhanced sensitivity to the inhomogeneous spin interactions [20]. For example, for the Zeeman Hamiltonian of the form, $H_{inh} = -\delta I_z$, where δ is the off-resonance and I_z is the z component of the total spin operator $\vec{I}$, the encoding of the MQ coherence of order p is $\exp(\pm i p \delta \tau)$, where τ is the duration of the coherences evolution. Therefore, the chemical shift separation between spectral lines as well as the effects of the field gradients is amplified by the coherence order.

The encoding the MQ coherences by homonuclear dipolar and quadrupolar couplings is more complex than that of the inhomogeneous interactions. The sensitivity of the double-quantum versus single-quantum (SQ) spinning-sideband patterns with respect to the dipolar couplings was analyzed for the case of magnetically equivalent spin-1/2 pairs under magic angle sample spinning (MAS) conditions in [21]. Comparing the relationships that describe the SQ and DQ free induction decays under MAS it was evident that the functional dependence of the dipolar coupling is different. The sensitivity of the spinning-sideband patterns to a variation of the dipolar coupling was estimated from the second and fourth van Vleck moments in the fast MAS regime for the creation of the DQ coherences by the BABA pulse sequence [22]. It was shown that for a number of BABA cycles higher than two the sensitivity to dipolar couplings is higher for DQ than for SQ van Vleck moments [21].

The goal of this paper is to investigate the possibility to obtain an enhanced sensitivity to the changes in the values of residual dipolar couplings by measurements of the higher-order multiple-quantum coherences for static samples with a complex ^{1}H dipolar coupling network like elastomers. The relative changes in the amplitude of ^{1}H DQ and TQ coherences of an isolated CH$_3$ group were evaluated theoretically in the absence of relaxation processes. It was shown that the relative variation of the TQ filtered NMR signal is higher than that of the corresponding DQ filtered signal. For a quadrupolar nucleus with spin $I = 2$ the sensitivity enhancements were simulated by considering four-quantum, triple-quantum, and double-quantum buildup curves. The predictions of the simulations were verified by the measurements of buildup curves of ^{1}H DQ, TQ, and four-quantum (FQ) filtered signals of differently cross-linked natural rubber samples.

2. Simulation of the sensitivity of MQ filtered signals to spin interactions

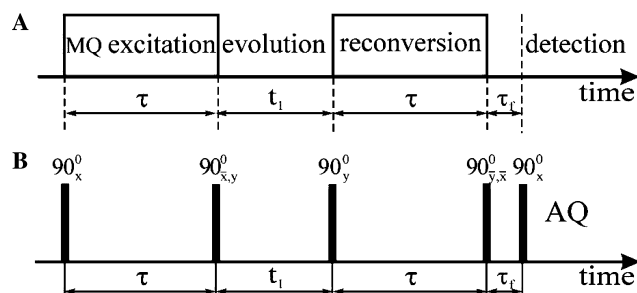In the following we shall consider the spin system response to the pulse sequence depicted in Fig. 1. This

Fig. 1. (A) General scheme for multiple-qauntum (MQ) spectroscopy. For short MQ coherences evolution times t_1 and variable excitation/reconversion time τ, MQ buildup curves are generated. A z-filter of duration t_f is incorporated in the scheme. (B) Five-pulse sequence used for excitation of even-order and odd-order MQ coherences. In the former case the phase of the excitation pulses are the same, in the latter case they differ by 90°. The reconversion period are composed of radio-frequency pulses with the phases orthogonal to the excitation pulses to generate a time-reversed dipolar DQ Hamiltonian.

pulse sequence can excite even- and odd-order MQ coherences that can be separated by phase cycling [20]. Even if the residual dipolar couplings are weak the multi-spin interactions are present in elastomers and other soft solids [2]. To drastically simplify the many-body problem we shall consider two types of spin systems: one is represented by an isolated methyl group and the second one by a fictitious nucleus with spin $I = 2$ with an axially symmetric quadrupole interaction attached to a polymer strand. For these cases the density matrix formalism can be used to evaluate the spin systems response to the radio-frequency pulses of Fig. 1 and finally to simulate the sensitivity of various orders of MQ coherences to the changes in the residual dipolar or quadrupolar couplings.

2.1. Residual spin interaction Hamiltonians

A simple model to describe the NMR spin system response consists of a single polymer chain between two network junction points [1,23]. The chain is considered to carry many NMR-active bonds. The multispin dipolar interaction between the protons along the chain—preaveraged by the fast segmental motions—can be written in the secular approximation [1,7]

$$\overline{H}_d = \sum_{i>j}(-\sqrt{6})D^{ij}\overline{P}_2(\cos\beta^{ij})T_{2,0}^{ij}, \tag{1}$$

where the dipolar coupling constant

$$D^{ij} = \left(\frac{\mu_0}{4\pi}\right)\gamma^2\hbar\left(\frac{1}{r_{ij}^3}\right),$$

of the ij spin-pairs depends on the internuclear distance r_{ij}. The bar in Eq. (1) represents the time average over the molecular reorientation process which is faster than the spin-precession period in the local dipolar field of the rigid lattice. This averaging by rapid segmental motions

is referred to as "pre-averaging" [1]. The angle β^{ij} is the angle between the internuclear vector $\vec{r}_{ij}$ and the direction of the main magnetic field. $\vec{B}_0$. $\overline{P}_2$ is the pre-averaged, second-order Legendre polynomial. $T_{2,0}^{ij}$ is the irreducible tensor operator describing the spin part of the secular dipolar coupling [10].

The residual dipolar interactions described by the Hamiltonian (Eq. (1)) can be evaluated by using the scale-invariant polymer model [1]. In this model, the dipolar interactions are averaged over all conformations of an intercross-link chain subject to the constraint that the end-to-end vector $\vec{R}$ is fixed. For such a chain the residual dipolar coupling may be expressed as [1,9]

$$\overline{H}_d = (-\sqrt{6})\frac{k}{N^2 a^2}\vec{R}^2 P_2(\cos\beta)\sum_{i>j} D^{ij}S^{ij}T_{2,0}^{ij}. \tag{2}$$

The dynamic order parameter is given by $S^{ij} \equiv \overline{P}_2[\cos\beta^{ij}(t)]$, where $\beta^{ij}(t)$ is the instantaneous angle between a given internuclear vector $\vec{r}_{ij}$ and $\vec{R}$. Under the pre-averaging condition, this angle denoted by β can be considered to define the direction of the end-to-end vector $\vec{R}$ with respect to $\vec{B}_0$. A scaled dynamic order parameter can be defined as $S_s^{ij} \equiv S^{ij}/N_e$, where the effective number of statistical segments is $N_e \equiv N/k$. The site selective dynamic order parameter S^{ij} takes into account the existence of the segmental dynamic heterogeneities along the polymer chain. The geometrical factor k depends on the model which is adopted to describe the chain statistics and is equal to 3/5 for a chain of freely jointed segments [9]. If the length of the statistical segment is denoted by a, and the quantity $\vec{q}^2 = \vec{R}^2/Na^2$ that represents the dimensionless squared end-to-end vector is introduced in Eq. (2), we can write

$$\overline{H}_d = (-\sqrt{6})\vec{q}^2 P_2(\cos\beta)\sum_{i>j} D^{ij}S_s^{ij}T_{2,0}^{ij}, \tag{3}$$

or

$$\overline{H}_d = \sum_{i>j} \overline{\omega}_d^{ij} T_{2,0}^{ij}, \tag{4}$$

where $\overline{\omega}_d^{ij}$ is the residual dipolar coupling for a (ij) spin pair.

In a disordered polymer, the end-to-end vector is assumed to obey Gaussian statistics [23,24]. For instance, the statistical average (denoted by $\langle(\ldots)\rangle_{\vec{R}}$, see below) of the reduced squared end-to-end vector is given by $\langle\vec{q}^2\rangle_{\vec{R}} \approx 1$.

The spin system response cannot be evaluated exactly for a multi-spin Hamiltonian given by Eq. (3). To avoid this complex problem we shall consider the simplified case of a methyl group attach to the polymer chain. In a strong external magnetic field, the three ^{1}H nuclei of a CH$_3$ group which reorient fast relative to the NMR linewidth of rigid groups can be described by an energy-level scheme which contains the eigenstates, $A_{\pm 3/2}$, $A_{\pm 1/2}$, and $E_{\pm 1/2}^a$, and $E_{\pm 1/2}^b$ following the irreducible repre-

sentations of the cyclic point group C$_3$ [25]. The indices $\pm m$ denote the z components of the total nuclear spin. The NMR response of a spin system containing isolated reorienting triads of spin-1/2 nuclei have been analyzed by treating the three spins as a single spin-3/2 particle subjected to a quadrupolar interaction [26,27]. Therefore, in a fast internal rotation limit the excitation of MQ coherences of a spin-1/2 triad can be described by a spin-isomer of total spin $I = 3/2$. The fast axial rotation reduces the rigid dipolar couplings by a factor of 1/2 and makes the angular dependence of the dipolar Hamiltonian the same for all proton pairs.

Finally, the residual dipolar coupling for the rapidly rotating spin triad is given by

$$\overline{H}_d^{(CH_3)} = \frac{(\sqrt{6})}{4} D^{(CH_3)} S^{(CH_3)} \frac{k}{N^2 a^2}\vec{R}^2 P_2(\cos\beta) T_{2,0}$$
$$\equiv \varpi_d^{(CH_3)} T_{2,0}. \tag{5}$$

Here, the dipolar coupling constant is defined by

$$D^{(CH_3)} = \left(\frac{\mu_0}{4\pi}\right)\gamma^2\hbar\left(\frac{1}{r^3}\right),$$

where r is the distance between the methyl protons ($r = 0.19$ nm). The number of statistical segments is denoted by N. The methyl order parameter $S^{(CH_3)}$ is given by the average of the second-order Legendre polynomial the argument of which contains the cosine of the angle between the instantaneous orientation of the C$_3$ axis and the end-to-end vector $\vec{R}$. The irreducible spin tensor operator $T_{2,0} = \frac{1}{\sqrt{6}}[3I_z^2 - I(I+1)]$ corresponds to a quasi-particle with spin quantum number $I = 3/2$ [28].

We are interested also (see below) in the MQ coherences produced by the irradiation of a nucleus with an axially symmetric quadrupole interaction attached to a polymer strand. For convenience we chose a fictitious quadrupolar nucleus with $I = 2$. The residual quadrupolar Hamiltonian is given by

$$\overline{H}_Q = \varpi_Q T_{2,0}, \tag{6}$$

where the residual quadrupolar coupling constant ϖ_Q has the same dependence on the end-to-end vector and angle β as the dipolar coupling (cf. Eq. (5)).

2.2. Isolated CH$_3$ group

The total spin coherence of a CH$_3$ group is represented by a TQ coherence. The NMR response of a static spin system can easily be evaluated in the density matrix formalism described in [10] by employing the specific irreducible tensor operator algebra [28]. In the absence of transverse relaxation the normalized NMR filtered signals from DQ coherences and TQ coherences are given by

$$S_{DQ}(\tau) = \frac{3}{5}\langle\langle\sin^2(\sqrt{6}\varpi_d^{(CH_3)}\tau)\rangle\rangle, \tag{7}$$

and

$$S_{TQ}(\tau) = \frac{9}{40} \langle\langle (\cos(\sqrt{6}\varpi_d^{(CH_3)}\tau) - 1)^2 \rangle\rangle. \quad (8)$$

In the above equations the symbol $\langle\langle\rangle\rangle \equiv \langle\langle\rangle_\Omega\rangle_R$ represents the ensemble average over the distribution of end-to-end vector lengths and the powder average of the angular part of the residual dipolar coupling in the disordered polymer network. We point out that Eqs. (7) and (8) can be used to compare the sensitivity of the DQ and TQ to the changes in the residual dipolar couplings.

2.3. Axially symmetric quadrupole interaction of a nucleus with spin $I = 2$

In order to investigate higher-order of MQ coherences we consider the simple case of a nucleus $I = 2$ with axially symmetric quadrupolar interaction. For such case the total spin coherence is represented by the fourth-order (FQ) coherences. This mimics qualitatively the NMR response of four spins with $I = 1/2$ coupled by dipolar interactions.

The normalized filtered signals from DQ, TQ, and FQ coherences can be evaluated with the results of [28] and are given by

$$S_{DQ}(\tau) = \frac{3}{35} \langle\langle (\sin(\sqrt{6}\varpi_Q\tau) + \sin(3\sqrt{6}\varpi_Q\tau))^2 \rangle\rangle, \quad (9)$$

$$S_{TQ}(\tau) = \frac{9}{40} \langle\langle (\cos(\sqrt{6}\varpi_Q\tau) - \cos(3\sqrt{6}\varpi_Q\tau))^2 \rangle\rangle, \quad (10)$$

and

$$S_{FQ}(\tau) = \frac{1}{20} \langle\langle (3\sin(\sqrt{6}\varpi_Q\tau) - \sin(3\sqrt{6}\varpi_Q\tau))^2 \rangle\rangle. \quad (11)$$

Eqs. (9)–(11) as well as Eqs. (7) and (8) have been derived using a program written in C++ that analytically evaluates the MQ coherences at different moments of time after the action of pulses and free evolution periods. The tensor algebra discussed in [28] was implemented in this program.

2.4. Simulation of the sensitivity of MQ buildup curves to the spin interactions

For the case of a methyl group the buildup curves of DQ and TQ coherences were evaluated using Eqs. (7) and (8). The average over the end-to-end vector was performed numerically using a Gaussian distribution function. The powder average was also executed numerically. These simulations are shown in Fig. 2 for the case of two cross-linked samples (A and F) of synthetic polyisoprene (see [10]). The scaled dynamic order parameters $S_s^{(CH_3)} \equiv S^{(CH_3)}/(N/k)$ of the methyl groups of samples A and F were estimated from experimental data to be $S_{s,A}^{(CH_3)} = 0.014$ and $S_{s,F}^{(CH_3)} = 0.036$ [10].
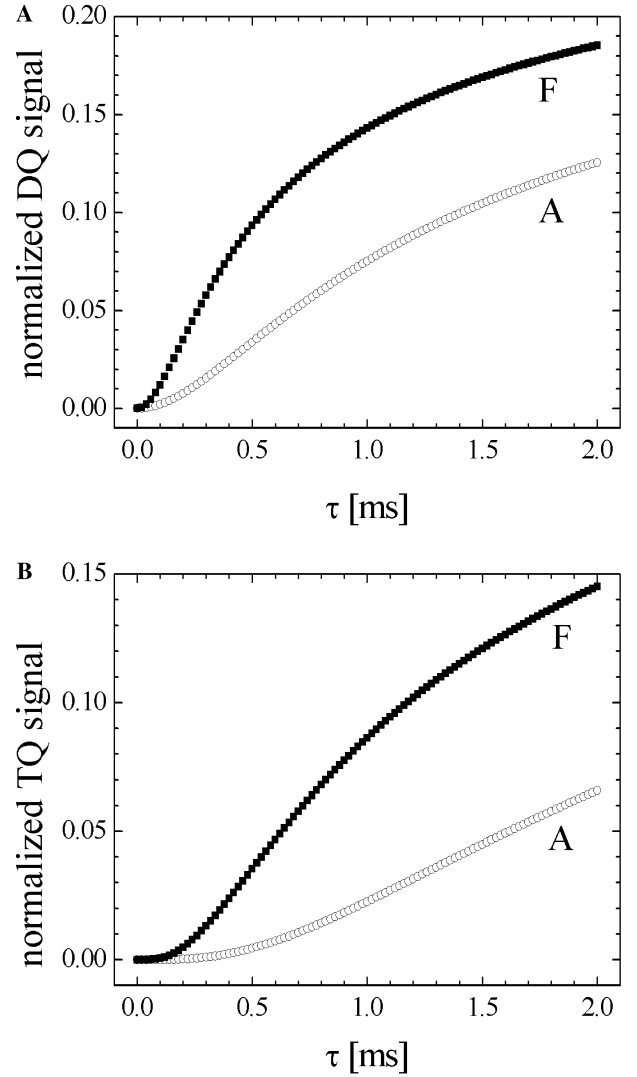

Fig. 2. Simulations of normalized double-quantum (A) and triple-quantum (B) buildup curves following Eqs. (7) and (8), and using the proton residual dipolar couplings of two synthetic 1,4-*cis*-polyisoprene, samples A and F with different cross-link density from [10]. For samples A and F the proton scaled dynamic order parameters are $S_{s,A}^{(CH_3)} = 0.014$ and $S_{s,F}^{(CH_3)} = 0.036$, respectively [10].

A relative sensitivity to the changes in the value of the residual dipolar couplings can be defined by the ratio $(S_F(\tau) - S_A(\tau))/S_A(\tau)$ which is related to the strength of the DQ and TQ filtered NMR signals denoted by $S(\tau)$, and taken at the same excitation/reconversion parameter τ for the samples A and F. This ratio is shown in Fig. 3A for τ values taken in the initial excitation/reconversion regime. It is evident that the TQ coherences are about three times more sensitive to the changes in the values of the residual dipolar couplings for $\tau \approx 0.03$ ms compared to the DQ buildup curves. The largest enhanced sensitivity of TQ buildup curves is present for small values of τ. Unfortunately, in this regime the signal-to-noise ratio of the TQ filtered signal is low.
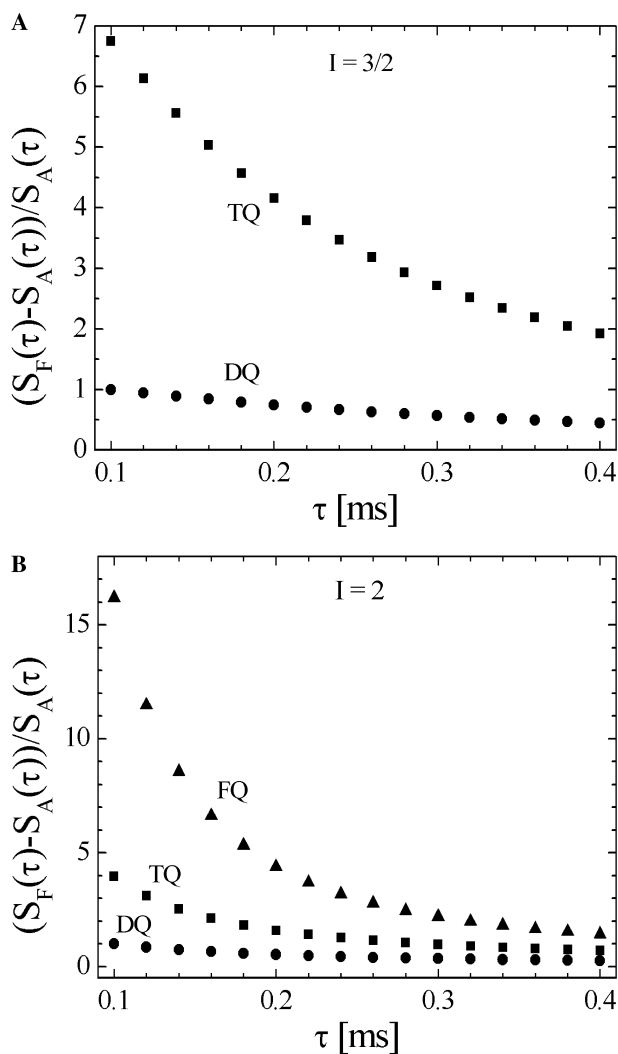
Fig. 3. The relative sensitivity $(S_F(\tau) - S_A(\tau))/S_A(\tau)$ to the residual dipolar couplings as a function of the excitation/reconversion time τ. (A) The simulated values of the methyl group with effective spin $I = 3/2$ for the DQ and TQ coherences. (B) Values for the DQ, TQ, and FQ coherences of a fictitious quadrupolar nucleus with spin $I = 2$. The values were normalized to the sensitivity parameter of the DQ coherences taken at the shortest τ.

For a fictitious quadrupolar nucleus with spin $I = 2$ the τ dependence of the sensitivity ratio is obtained from Eqs. (9)–(11) for the FQ, TQ, and DQ buildup curves. The values of the residual quadrupolar couplings used in the simulations correspond to those of the residual dipolar couplings of the polyisoprene samples A and F. The resultant sensitivity ratios are shown in Fig. 3B. The four-quantum coherences are almost one order of magnitude more sensitive to the changes in the spin interactions than the DQ coherences in the initial excitation regime. This sensitivity decreases appreciably with increasing τ but is still larger than the sensitivity of the TQ and DQ coherences.

3. Experimental

3.1. Materials

The investigated type of elastomer is based on commercially available natural rubber (NR) SMR10 (Malaysia). As additives, the samples of the cross-linked NR series contain 3 phr (parts-per-hundred-rubber) ZnO and 2 phr stearic acid. Three differently cross-linked samples were investigated. The sulfur and accelerator contents are shown in Table 1. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butyl-sulfenamide). After mixing the compounds in a laboratory mixer at 50 °C, the vulcanization was performed at 160 °C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus (G) at the temperature of 160 °C in the vulcameter directly after the vulcanization. The measurements were performed with oscillation amplitude of $\pm 0.5°$ and a frequency of 1.67 Hz. The values of G and Young modulus E are shown in Table 1 for the cross-linked NR series.

3.2. NMR Experiments

The NMR experiments were performed at a ^{1}H frequency of 299.87 MHz on a Bruker DMX-300 spectrometer. Even order multi-quantum buildup curves were measured using the five-pulse sequence $(90°_{x+\phi} - \tau - 90°_{\bar{x}+\phi}) - t_1 - (90°_y - \tau - 90°_{\bar{y}}) - \tau_f - 90°_x - t_2$ [20] (Fig. 1). For odd-order MQ coherences the pulse sequence $(90°_{x+\phi} - \tau - 90°_{y+\phi}) - t_1 - (90°_y - \tau - 90°_{\bar{x}}) - \tau_f - 90°_x - t_2$ was used [20]. The phase cycling scheme used for detection of the MQ coherences of the order $\pm p$ is described in [20]. The change in the phases of the MQ excitation pulses is $\Delta\phi = 2\pi/|p|$, where a value of $p = \pm 6$ was chosen. The maximum MQ coherences detected in the sample series was $p = \pm 4$. The signal-to-noise ratio of MQ coherences of orders $p = \pm 5$ and $p = \pm 6$ was very low. The MQ excitation pulse programs were written in a way to produce $2p$ separate data files each corresponding to one step in the phase cycle. These files were suitably processed so that the signals various orders of MQ coherences are obtained. A 13 µs 90° pulse, and a 1 s recycle delays were used. The MQ evolution time and the z-filter delay were fixed to $t_1 = 20$ µs and $\tau_f = 20$ µs, respectively.

Table 1
Properties of the series of cross-linked NR samples

Sample	Sulfur-accelerator content (phr)	Shear modulus[a] G (dNm)	Young modulus[a] E (MPa)
NR1	1–1	5.2	0.9
NR4	4–4	13.2	2.1
NR7	7–7	16.2	2.8

[a] The uncertainties are less than 10%.

4. Results and discussion

To investigate the sensitivity of the MQ coherences to the changes in the ^{1}H residual dipolar couplings in the initial regime of excitation/reconversion a cross-link natural rubber series (cf. Table 1) were measured. In natural rubber the proton dipolar network is rather complex being extended along the polymer chains [10,19]. The residual dipolar couplings between different functional groups are difficult to be evaluated from first principles. Therefore, a quantitative theoretical estimation of the MQ buildup curves and their sensitivity to the variation of residual dipolar couplings will not be discussed. Nevertheless, in the following an empirical approach is presented.

The fact that the multi-quantum coherences could only be detected up to fourth order can be related to the small values of the ^{1}H residual dipolar couplings and the low pumping efficiency of the five-pulse sequence. The normalized buildup curves for ^{1}H DQ, TQ, and FQ coherences are shown in Fig. 4 for the three samples (see Table 1). The intensity of the FQ filtered signals is about two orders of magnitude smaller than the DQ signals (cf. Figs. 4A and C). Moreover, the TQ buildup curves have a relatively good signal-to-noise ratio from which reliable fits can be obtained (cf. Figs. 4A and B). It is already obvious from Fig. 4 that for the values of τ taken in the initial regime of the excitation/reconversion periods, where the effect of transverse relaxation can be neglected in a good approximation, the dispersion in the signals as a function of cross-link density increases with the MQ order. This is in a full agreement with the simulations discussed above (see Figs. 2 and 3).

A sensitivity parameter to the residual dipolar couplings can be defined by the ratio $(S_{NR7}(\tau) - S_{NR1}(\tau))/S_{NR1}(\tau)$. This ratio can be evaluated from the MQ buildup curves of Fig. 4 and depends on the MQ excitation/reconversion parameter τ. The sensitivity parameters evaluated from DQ, TQ, and FQ buildup curves of Fig. 4 are shown in Fig. 5 as a function of τ for the initial region of the buildup curves. It decreases for longer values of τ in qualitative agreement with the simulations shown in Fig. 3. The measured sensitivity parameter is almost five times larger for FQ coherence than that for DQ coherence. That clearly proves the increase in sensitivity of the higher-order of MQ coherences to the changes in the values of the dipolar couplings. This is again supported by the simulations shown in Fig. 3B for the case of a quadrupolar nucleus.

In the above discussions the effect of transverse relaxation on the MQ filtered signals was neglected. This approximation is justified in the initial regime of excitation/reconversion periods. Only in such conditions the residual spin couplings can be measured model free. At longer values of excitation times τ the transverse relaxation starts to encode the MQ filtered signals [10].
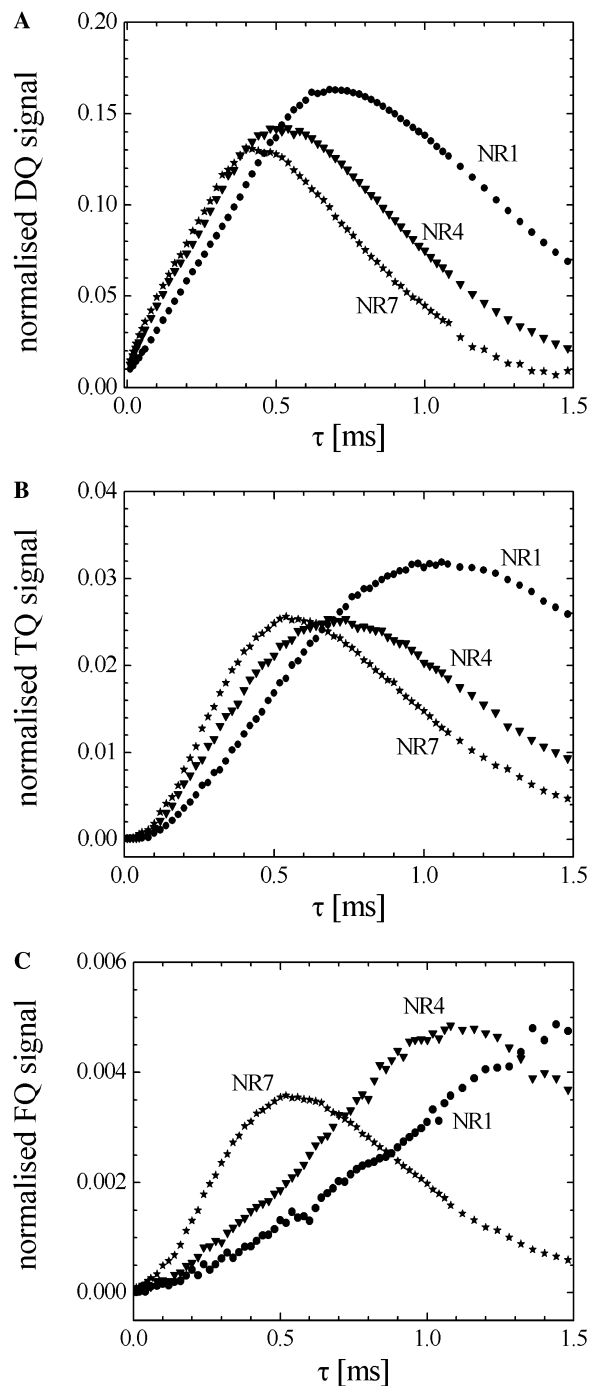

Fig. 4. Experimental ^{1}H DQ (A), TQ (B), and FQ (C) buildup curves for samples NR1, NR4, and NR7 (cf. Table 1). The MQ signals are normalized to the integral intensity of the ^{1}H single-quantum spectrum.

Transverse magnetization relaxation measured by solid-, stimulated-, and magic-echoes [1,4–7] are also sensitive to the changes in the residual dipolar or quadrupolar couplings via residual spin interactions and segmental motions. Therefore, the encoding of the MQ filtered signals by transverse relaxation and residual spin interactions is complex and cannot easily be evaluated.
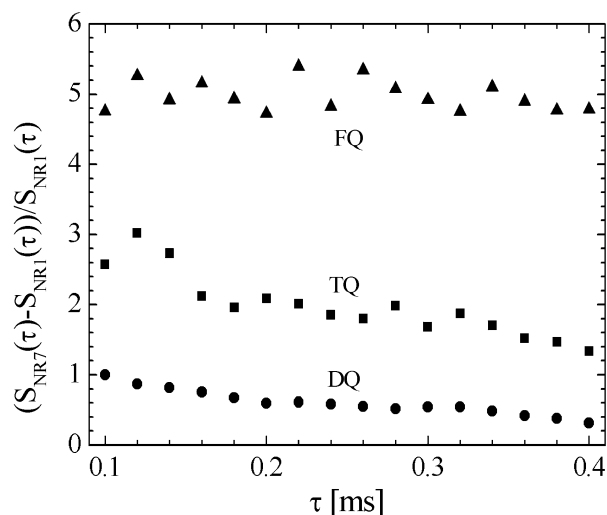
Fig. 5. Sensitivity parameter $(S_{NR7}(\tau) - S_{NR1}(\tau))/S_{NR1}(\tau)$ a function of τ in the initial region of the DQ, TQ, and FQ buildup curves evaluated from the measured MQ buildup curves of Fig. 4. The values were normalized to the sensitivity parameter of the DQ coherences taken at the shortest τ.

5. Conclusions

The development of the NMR methods which exhibit an increased sensitivity to the changes in the residual dipolar or quadrupolar couplings for elastomer systems in different states described by internal or external parameters represents an important topic of research aimed of improving quality control of rubber materials. The measurement of high-order coherences proves to be a method to enhance the sensitivity of the spin system response to changes in dipolar and quadrupolar couplings.

The possibility to excite ^{1}H high-order coherences in elastomers is due to the existence of the multi-spin dipolar network extended mainly along the polymer chain [2] (and references therein). In selecting the appropriate order of MQ coherences a trade-off between the gain in sensitivity and the reduction in the signal-to-noise ratio with the increase in the order of the MQ coherences has to be taken into account for each particular polymer. It is noted that this method can benefit from the sensitivity enhancement of measuring MQ coherences by the Carr–Purcell–Meiboom–Gill (CPMG) detection scheme proposed recently in the group of Pines and co-workers [29].

References

[1] J.-P. Cohen Addad, NMR and fractal properties of polymeric liquids and gels, Prog. NMR Spectrosc. 25 (1993) 1–312.

[2] D.E. Demco, S. Hafner, H.W. Spiess, Multidimensional NMR techniques for the characterization of viscoelastic materials, in: V.M. Litvinov, P.P. De (Eds.), Handbook of Spectroscopy of Rubbery Materials, Rapra Technology Ltd, Shawbury, 2002.

[3] G. Navon, H. Shinar, U. Eliav, Y. Seo, Multiquantum filters and order in tissues, NMR Biomed. 14 (2001) 112–132.

[4] J. Collignon, H. Sillescu, H.W. Spiess, Pseudo-solid echoes of proton and deuteron NMR in polyethylene melts, Colloid Polym. Sci. 259 (1981) 220–226.

[5] P.T. Callaghan, E.T. Samulski, Molecular ordering and the direct measurement of weak proton–proton dipolar interactions in a rubber network, Macromolecules 30 (1997) 113–122.

[6] R. Kimmich, NMR: Tomography, Diffusiometry, Relaxometry, Springer-Verlag, Berlin, Heidelberg, New York, 1997, and references therein.

[7] R. Fechete, D.E. Demco, B. Blümich, Chain orientation and slow dynamics in elastomers by mixed magic-Hahn echo decays, J. Chem. Phys. 118 (2003) 2411–2421.

[8] D.E. Demco, S. Hafner, C. Fülber, R. Graf, H.W. Spiess, Two-dimensional proton magnetization-exchange NMR spectroscopy in cross-linked elastomers, J. Chem. Phys. 105 (1996) 11285–11296.

[9] P. Sotta, C. Fülber, D.E. Demco, B. Blümich, H.W. Spiess, Effect of residual dipolar interactions on the NMR relaxation in cross-linked elastomers, Macromolecules 29 (1996) 6222–6230.

[10] M. Schneider, L. Gasper, D.E. Demco, B. Blümich, Residual dipolar couplings by ^{1}H dipolar-encoded longitudinal magnetization, double- and triple-quantum nuclear magnetic resonance in cross-linked elastomers, J. Chem. Phys. 111 (1999) 402–415.

[11] R. Fechete, D.E. Demco, B. Blümich, Macromolecules, segmental anisotropy in strained elastomers by ^{1}H NMR of multipolar spin states, Macromolecules 35 (2002) 6083–6085.

[12] M. Wang, M. Bertmer, D.E. Demco, B. Blümich, V.M. Litvinov, H. Barthel, Indication of heterogeneity in chain-segment order of a PDMS layer grafted onto a silica surface by ^{1}H multiple-quantum NMR, Macromolecules 36 (2003) 4411–4413.

[13] R.S. Maxwell, B. Balazs, Residual dipolar coupling for the assessment of cross-link density changes in γ-irradiated silica PDMS composite materials, J. Chem. Phys. 116 (2002) 10492–10502.

[14] K. Saalwächter, P. Ziegler, O. Spyckerelle, B. Haidar, A. Vidal, J.-U. Sommer, ^{1}H multiple quantum nuclear magnetic resonance investigations of molecular order distributions in poly(dymethylsiloxane) networks: evidence of a linear mixing law in bimodal systems, J. Chem. Phys. 116 (2003) 3468–3478.

[15] A. Wiesmath, C. Filip, D.E. Demco, B. Blümich, Double-quantum-filtered NMR signals in inhomogenous magnetic fields, J. Magn. Reson. 149 (2001) 258–263.

[16] D.E. Demco, R. Fechete, B. Blümich, Residual dipolar couplings of soft solids by accordion magic sandwich, Chem. Phys. Lett. 375 (2003) 406–412.

[17] C. Malveau, P. Tekely, D. Canet, Visualization of residual anisotropic interactions in crosslinked natural rubbers by dipolar local field measurements and ^{2}H natural abundance NMR spectroscopy, Solid State Nucl. Magn. Reson. 7 (1997) 271–280.

[18] T. Fritzhanns, D.E. Demco, S. Hafner, H.W. Spiess, Multidimensional ^{1}H NMR nuclear Overhauser spectroscopy under magic angle spinning: theory and application to elastomers, Mol. Phys. 97 (1999) 931–943.

[19] R. Graf, D.E. Demco, S. Hafner, H.W. Spiess, Selective residual dipolar couplings in cross-linked elastomers by ^{1}H double-

quantum NMR spectroscopy, Solid State Nucl. Magn. Reson. 12 (1998) 139–152.

[20] M. Munowitz, A. Pines, Principles and applications of multiple-quantum NMR, Adv. Chem. Phys. 66 (1987) 1–145.

[21] R. Graf, D.E. Demco, J. Gottwald, S. Hafner, H.W. Spiess, Dipolar couplings and internuclear distances by double-quantum nuclear magnetic resonance spectroscopy of solids, J. Chem. Phys. 106 (1997) 885–895.

[22] M. Feike, D.E. Demco, R. Graf, J. Gottwald, S. Hafner, H.W. Spiess, Broadband multiple-quantum NMR spectroscopy, J. Magn. Reson. A 122 (1996) 214–221.

[23] M. Rubinstein, R. Colby, Polymer Physics, Oxford University Press, New York, 2003.

[24] A.Y. Grosberg, A.R. Khokhov, Statistical Physics of Macro-molecules, American Institute of Physics, Woodbury, NY, 1994.

[25] P.S. Allen, W. Harding, P. Mansfield, J. Phys. C 5 (1972) L80.

[26] Y.N. Moskvich, N.A. Sergeev, G.I. Dotsenko, Phys. Status Solidi A 30 (1975) 409.

[27] U. Friedrich, I. Schnell, D.E. Demco, H.W. Spiess, Chem. Phys. Lett. 285 (1998) 49.

[28] G.J. Bowden, W.D. Hutchison, J. Khachan, J. Magn. Reson. 67 (1986) 415–437.

[29] K.H. Lim, T. Nguyen, T. Mazur, D.E. Wemmer, A. Pines, Sensitivity enhancement in multiple-quantum NMR experiments with CPMG detection, J. Magn. Reson. 157 (2002) 160–162.