Segmental Anisotropy in Strained Elastomers by ^{1}H NMR of Multipolar Spin States

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Introduction. A well-known consequence of the theory of rubber elasticity is bond orientation.[1,2] Deformation of an elastomer induces anisotropy of the backbone bonds of the polymer coil. In recent NMR studies of rubber elasticity the mechanism of deformation and the orientation of network chains has received increasing attention. One- and two-dimensional NMR spectroscopy of ^{2}H and ^{1}H has been used intensively in the past decade to measure the dipolar correlation effect, homonuclear and heteronuclear residual dipolar couplings, and corresponding dynamic order parameters.[3−6]

In the presence of a uniaxial mechanical force the deuterium NMR line splits, revealing that a molecular anisotropy of the chain segments is induced in the polymer network.[7−14] There are two distinct mechanisms responsible for this induced local anisotropy:[10,12] (i) The anisotropy of the residual dipolar interactions is increased for each chain due to changes in the length and orientation of the network junctions and is independent of the interactions between the chains. (ii) The second mechanism responsible for the chain anisotropy is given by the isotropic short-range orientational interactions between segments belonging to different chains. Under the axial deformation the chains will produce a screened short-range excluded-volume interaction with an induced attractive potential.

Besides ^{2}D NMR, other NMR methods used for investigation of the residual dipolar couplings in stretched natural rubber bands are based on ^{1}H Hahn and solid echoes,[15,16] the stimulated echo,[5] and ^{1}H double-quantum (DQ) coherences and dipolar encoded longitudinal magnetization (DELM).[17,18] The latter multipolar spin states can be easily understood for the case of dipolar coupled spin-$^1/_2$ pairs. The evaluation of the spin system response in this case shows that the density operator at the end of DQ excitation period contains a term of the form $(I_{z1} + I_{z2}) \sin(D_{DQ}\tau)$, where I_{zi} $(i = 1, 2)$ are the z components of the spin vector operator, D_{DQ} is the dipolar coupling constant edited by the DQ experiment, and τ is the duration of the excitation period.[17,18] Determination of ^{1}H and ^{2}H residual dipolar and quadrupolar interactions by multipolar spin states (like DQ and DELM) and line splitting are model free compared to the methods based on dipolar correlation functions.[5,15,16] By measuring the residual dipolar couplings vs the extension ratio λ and its dependence on the orientation angle θ, where θ is the angle between the uniaxial applied force $\bar{F}$ and the static magnetic field direction $\bar{B}_0$, it is possible to distinguish the influences from chain stretching and from chain reorientation in the deformation process.[15]

In this paper, we report on the angular dependence of the ^{1}H residual dipolar couplings in stretched elastomers determined model free from the initial excitation regime of ^{1}H DELM decay and DQ coherence build-up curves.

Experimental Section. a. Materials. The system investigated is based on commercially available natural rubber (NR) SMR10 (Malaysia). As additives, the samples of the cross-link series contain 3 phr (parts per hundred rubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents of the sample are 2 phr each. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butylsulfenamide). The parameters of the vulcanization process are described in ref 17.

b. NMR Measurements. The NMR experiments were performed at a ^{1}H frequency of 200.025 MHz on a Bruker DSX-200 spectrometer. The DELM decay and DQ build-up curves were recorded with the pulse sequence presented in Figure 1.[17] The 90° pulse length was 13.5 μs, and recycle delays of 1 s were used. The evolution time and z filter delay were fixed to $t_1 = 50$ μs and $\tau_f = 5$ ms, respectively. A special Bruker NMR probe head (tilt coil) was used which allows the orientation of the resonator axis relative to the direction of the static magnetic field. A natural rubber band having a U-shape was stretched to the elongation ratio $\lambda \approx 3$ using a Teflon plate.

Results and Discussion. The ^{1}H DELM decays and DQ build-up curves were measured for a stretched NR sample, and the results are shown in parts a and b of Figure 2, respectively, for three angles θ. For the magic angle $\theta \approx 55°$ the DELM decay curve has the smallest decay (cf. Figure 2a). This is also valid for the DQ build-up curves (cf. Figure 2b) where the maximum (see dashed lines in Figure 2b) is reached for the longest excitation/reconversion times for $\theta \approx 55°$. This proves that a dominant contribution to the angular dependence of the residual dipolar couplings and transverse relaxation rates is related to the second-order Legendre polynomial $P_2(\cos\theta) = {}^1/_2(3\cos^2\theta - 1)$. Furthermore, this dependence is supported by the behavior of the curves for $\theta = 0°$ and $\theta = 90°$.

In the initial regime of short excitation/reconversion times τ defined by $||\bar{H}_d||\tau \ll 1$, where $||\bar{H}_d||$ is the norm of the residual dipolar Hamiltonian,[17] the normalized DELM and DQ filtered signals are given by[17]

$$\frac{S_{DELM}(2\tau;t_{1,2}=0)}{S_{DELM}(\tau=0;t_{1,2}=0)} \approx 1 - [D_{eff}^{DELM}]^2\tau^2 + ... \qquad (1)$$

and

$$\frac{S_{DQ}(2\tau;t_{1,2}=0)}{S_0} \approx [D_{eff}^{DQ}]^2\tau^2 - ... \qquad (2)$$

where S_0 is the integral intensity of the NMR signal after a 90° pulse. The time parameters τ, t_1, and t_2 are given in Figure 1. Effective residual dipolar couplings D_{eff}^{DELM} and D_{eff}^{DQ} are defined in ref 17. These quantities were determined from the data presented in Figures 2 using eqs 1 and 2 and are shown in Figure 3a. As discussed before,[17] for a cross-link series from synthetic 1,4-*cis*-polyisoprene $D_{eff}^{DELM} > D_{eff}^{DQ}$, which is also evident from Figure 3a. A minimum in the values of

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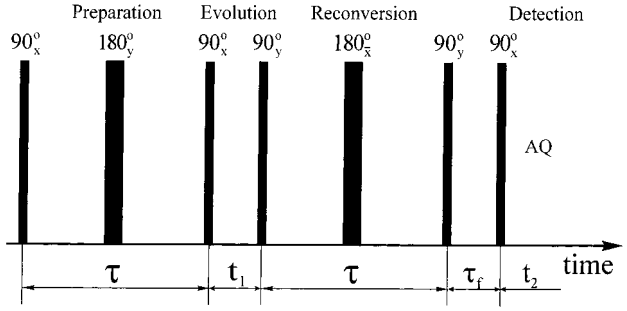

Figure 1. A five-pulse sequence supplemented by 180° refocusing pulses for measuring dipolar-encoded longitudinal magnetization decay and double-quantum build-up curves. The excitation, evolution, reconversion, *z* filter, and detection periods are denoted by τ, t_1, τ, τ_f, and t_2, respectively.

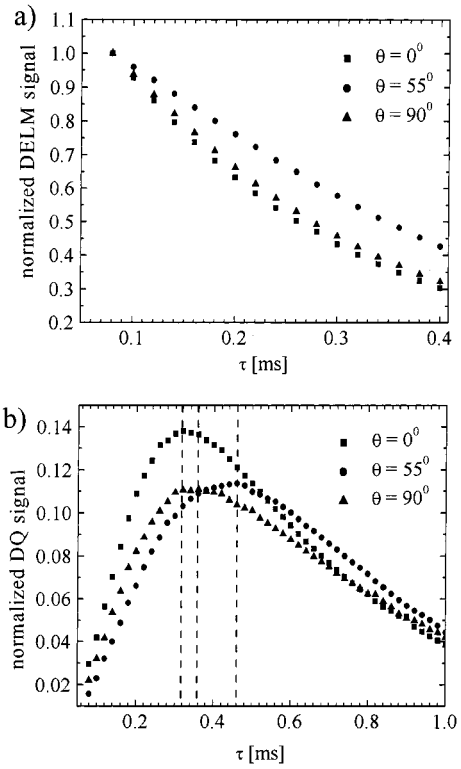

Figure 2. Normalized ^{1}H DELM (a) and DQ (b) filtered signals vs the excitation/reconversion times the orientation angles θ = 0°, 55°, and 90° between the uniaxial stretching force and the direction of the static magnetic field.

$D_{\text{eff}}^{\text{DELM}}$ and $D_{\text{eff}}^{\text{DQ}}$ exists for the magic angle (see dashed line in Figures 3). This minimum is not close to zero as expected if only a θ dependence of the residual dipolar couplings depending on $P_2(\cos\theta)$ is effective. The different dipolar networks edited by the DELM and DQ experiments are also evident from the normalized angular dependence of the residual dipolar couplings shown in Figure 3b. The angular orientation effect is enhanced for the DELM and DQ curves at longer τ values (cf. parts a and b of Figure 4). For DQ coherences this is valid for $\tau < \tau_{\max}$, where $\tau_{\max}$ corresponds to the maximum of the build-up curve. This is due to the fact that at these times the filtered signals are a function of $(D_{\text{eff}}^{\text{DELM}})^{2n}$ and $(D_{\text{eff}}^{\text{DQ}})^{2n}$, where n is an integer number. Moreover, the transverse relaxation starts to affect the signal evolution.[17] This process is also θ dependent.[15]

Conclusions. The investigation of segmental anisotropy by sample orientation can be performed easily together with a variation of the elongation ratio. The use of ^{1}H multipolar spin states like dipolar encoded

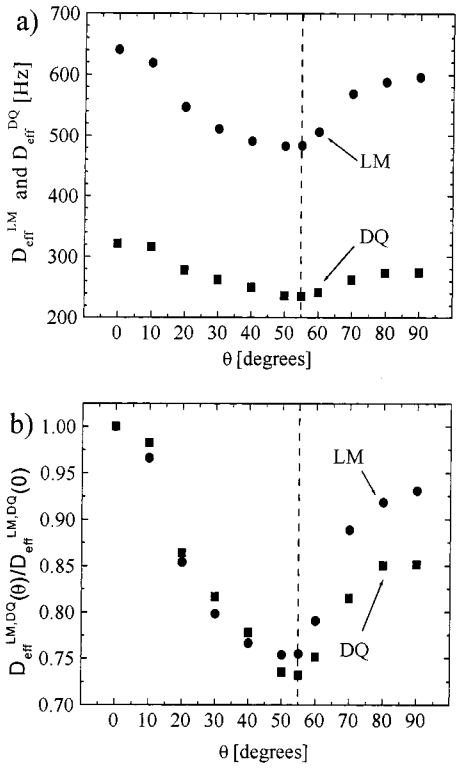

Figure 3. (a) Proton effective residual dipolar couplings measured from DELM decay and DQ build-up curves vs the orientation angle θ. (b) The normalized effective residual dipolar couplings are obtained from (a) as a function of angle θ.

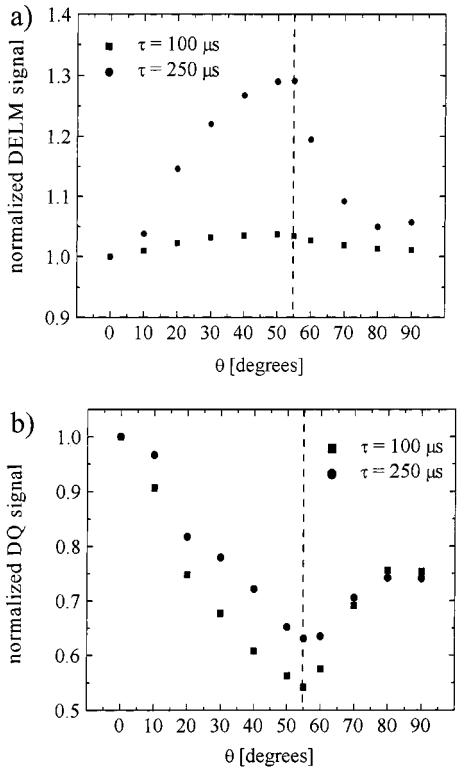

Figure 4. Normalized ^{1}H DELM (a) and DQ (b) filtered signals detected after the last 90° pulse in Figure 1 vs the orientation angles θ for two values of the excitation/reconversion times τ.

longitudinal magnetization and double-quantum coherences in the initial evolution regime allows measurements of residual dipolar couplings without contributions from the dipolar correlation effect and without need for chain deuteration. Therefore, investigations of chain deformation and interactions by using these methods become more simple. Further work along these lines is in progress.

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