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Local order and strain-induced orientation in poly(butadiene) networks studied by ^{2}H NMR

Heike Menge[1,*], Piyasiri Ekanayake[1], Mike E. Ries[2], M. G. Brereton[2], Matthias Findeisen[3]

[1] Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, Friedemann-Bach-Platz 6,
D-06108 Halle/Saale, Germany
[2] IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK
[3] Universität Leipzig, Fakultät für Chemie und Mineralogie, Institut für Analytische Chemie,
Lineé-Strasse 3, D-04103 Leipzig, Germany

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Summary

Deuterium nmr has been employed to determine the average orientation of chain segment in poly(butadiene) networks. The nmr spectrum lineshape reveals the orientation distribution of network vectors due to the crosslinks, whereas the observed splitting gives information about the orientation due to segmental interactions. Both the lineshape and the splitting have been fitted simultaneously for a range of deformed poly(butadiene) networks varied in crosslink density and precursor chain length. From the fitting parameters the separate contribution to the average orientation arising from network constraints and interaction are calculated. These are used to estimate the effective molecular weight between topological constraints and the size of the segmental interaction. It could be shown that the latter remains constant as the crosslink density is varied. This is a strong evidence of the recently published theoretical framework.

Introduction

Rubbers are important materials for numerous and important applications. Nuclear magnetic resonance (nmr) allows one to relate macroscopic properties (such as elastic moduli) to microscopic behaviour of polymeric chains. One essential nmr property in elastomers is the presence of residual interactions, due to local order related to the constraints resulting from crosslink junctions. ^{2}H-nmr has been devoted to be a sensitive and powerfull tool to study this anisotropy at a molecular level in strained elastomers.

A number of deuterium (^{2}H) nmr studies in elastomers have been already performed (1-6). For undeformed rubbers a single resonance line is observed. Under uniaxial deformation the spectra splits into a well-defined doublet structure (7). A non-interacting Gaussian phantom network has been theoretically shown to generate no splitting under deformation (6,8,9). These results therefore indicate that to model the chain reorientation in a strained elastomer one must introduce chain interactions (6,10,11). In strained rubbers there is a higher degree of anisotropy than that merely induced by the crosslinks. Short-range orientational interactions between segments such as nematic interactions (10), steric interactions (11) and anisotropic junction fluctuations (12) are some of the proposed explanations for this extra degree of anisotropy. A theory by Brereton and Ries (11) attributes the higher degree of anisotropy implied by the splitting to the inter chain steric interactions. In a network a polymer segment interacts with many neighbouring ones. These interactions can effectively described by a mean field. Under deformation the distribution of monomeric segments generates, through their isotropic steric interactions, an anisotropic mean field. All chains within the rubbery matrix experience this perturbed mean field that subsequently causes an induced alignment with the

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[*] Corresponding author
e-mail: menge@physik.uni-halle.de

strain direction (11,13). The resultant splitting due to this interaction is dependent on the size of the excluded volume through the Edwards screening length (14,15). In a dry network it is this parameter with the rescaled quadrupolar constant that describes the observed ^{2}H nmr spectra as function of strain (11,13).

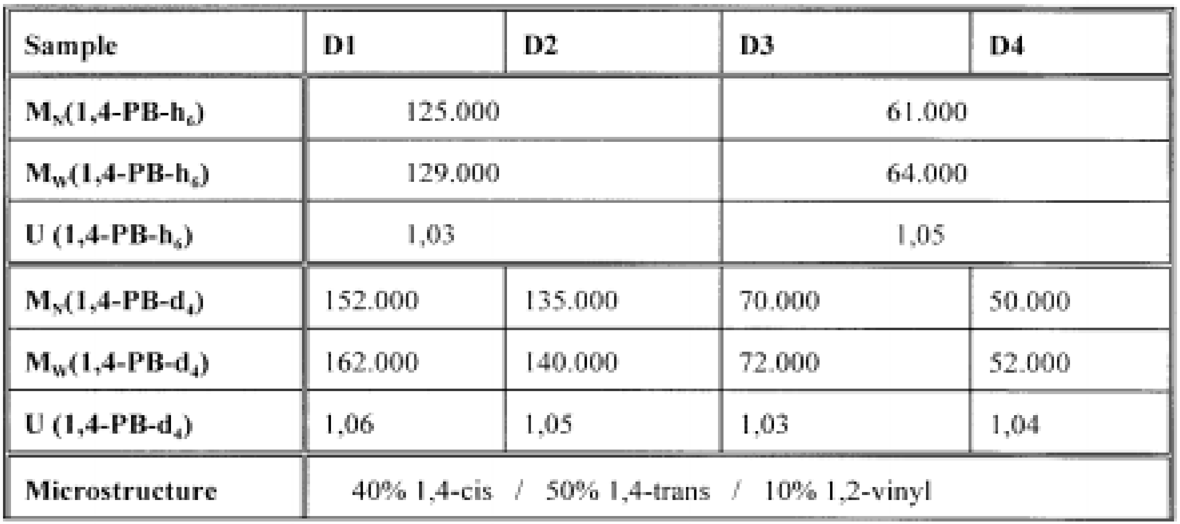
On the other hand, residual interactions in the relaxed state have been analysed. It was shown that dangling ends have an nmr behaviour which is different from that of elastic chains, leading to a two-component nmr signal. The strain-induced orientation and the residual interactions in the relaxed state, being both related to elastic properties of network chains, are expected to depend on the same molecular parameters. The signal from networks has a liquid-like component, which behaves isotropically in the relaxed state (6,7). This component in the nmr signal is attributed to dangling ends.

The aim of this paper is to proof this theoretical approach given in ref. (13) for samples with different crosslink densities.

Experimental

All experiments were carried out on a Varian Unity 400 widebore spectrometer at 61.3 MHz for deuterons and at room temperature. Spectra were obtained using a standard 90° rf pulse of approximate 7 µs. The deuteron measurements under mechanical deformation were performed by a simple stretching device parallel to the magnetic field. The stretching ratio λ ($=l/l_0$) was determined from the distance between two marks before and after stretching.

The elastomeric networks under study were based on partially CD_2-deuterated poly(butadiene) PB-d_4 with cis/trans/vinyl-microstructure, different molar mass of the precursor chains and a narrow mass distribution (see table 1).



Sample	D1	D2	D3	D4
M_N(1,4-PB-h_6)	125.000		61.000	
M_W(1,4-PB-h_6)	129.000		64.000	
U (1,4-PB-h_6)	1,03		1,05	
M_N(1,4-PB-d_4)	152.000	135.000	70.000	50.000
M_W(1,4-PB-d_4)	162.000	140.000	72.000	52.000
U (1,4-PB-d_4)	1,06	1,05	1,03	1,04
Microstructure	40% 1,4-cis / 50% 1,4-trans / 10% 1,2-vinyl			

table 1: characterisation of precursor poly(butadiene)

The position of deuteration was checked by {^{2}H} ^{13}C INEPT tripel resonance nmr experiment (standard 5mm tripel resonance probe) proposed by Rinaldi (16) using the BRUKER AVANCE DRX-400 spectrometer at the department of chemistry at Leipzig University. Based on the assignment given by Rinaldi (16) no other deuterons than the methylene groups have been observed in the detected spectra. The deuterated polymers were mixed in a ratio 1:9 with a corresponding commercial poly(butadiene) with nearly the same parameters. An amount of 0.5 phr (parts per hundred rubber) Dicumyl peroxide (DCP) was used as crosslinking agent for all networks under study here. The samples were vulcanised in a vulcameter press at 145 °C and 100 bar for 1h. The samples were characterised by mechanical and swelling measurements as well as by proton and deuteron transverse magnetisation decay. From the magnetisation decays the fractions of dangling ends, intercrosslink chains and the mean molar mass between two crosslinks M_C were determined using a two-component model described in detail in ref. (17). The results are published elsewhere (18).

Theory

The deuterium nucleus posses a non-zero electric quadrupolar moment and consequently an electrostatic energy in the non-uniform electric field of the carbon deuterium bond. The result is that the Zeeman levels of the nuclear spin are dependent on the orientation of this bond relative to the applied magnetic field. The motion of the carbon deuterium bond is assumed to follow rigidly that of the chain and thus allows NMR to be a monitor of polymer dynamics.

A scale invariant model consisting of a series of statistical units $\{b_j\}$ to represent the network chains was introduced by Cohen-Addad (19,20) and further developed by Brereton (21,22). The quadrupolar interaction is rescaled by rapid local reorientations onto this coarse-grained representative chain. The effect is to reduce the magnitude of the static quadrupole interaction strength and make the perturbations of the energy levels of the deuterium nuclei dependent on the instantaneous orientations of the statistical units. For a nucleus within a particular statistical segment $\mathbf{b}_j$ this orientation gives rise to a perturbation of the precessional Larmor frequency by $\Delta\omega(\mathbf{b}_j)$, which is written in ref (11) as

$$\Delta\omega(\mathbf{b}_j) = \nu_o \frac{2b_z^2 - b_y^2 - b_x^2}{b^2} \tag{1}$$

where $\{b_x^2, b_y^2, b_z^2,\}$ are the Cartesian co-ordinates of the labelled NMR statistical segment (average length b) and ν_0 is the rescaled interaction constant. To focus on the average orientation of the chain segments, it is more convenient to write this as

$$\Delta\omega(\mathbf{b}_j) = 2\nu_o P_2(\cos\theta) \tag{2}$$

where θ is the angle the applied magnetic field makes with the statistical bond vector $\mathbf{b}_j$ and $P_2(\cdots)$ is the second order Legendre polynomial.

In the regime where the local level bond dynamics are fast compared to the timescale set by ν_0^{-1} the relaxation of the transverse components of the magnetisation can be written (13, 22) as

$$G(t,\lambda) = \overline{\cos\left[2\nu_o\langle P_2(\cos\theta)\rangle t\right]} \tag{3}$$

The $\langle\cdots\rangle$ is a time average over all the available conformations of the nmr active bond subject to the network constraint imposed by the deformation λ through the crosslinks ("annealed average"), whilst the $\overline{(\cdots)}$ indicates an average over all possible network vectors (or crosslink points) ("quenched average").

For an *interacting network*, the important point is that there are two principle factors that influence the averaging over all the available conformations of the NMR active bond. Firstly there is the constraint caused by the junction points. The end-to-end vector formed by two consecutive crosslinks determines a static residual average orientation of the labelled bond. Secondly there are the interactions of the chain segments in the rubber with their many neighbours. The average orientation of an NMR active segment can be written as $\langle P_2(\cos\theta)\rangle_{\mathbf{R},V}$, where the subscript $\mathbf{R}$,V indicates that both the constraints of the network vector $\mathbf{R}$ and the interactions V have been included.

Each of the above two mentioned factors will contribute to the average orientation of the carbon deuterium bond. The effect of the network constraint on the orientation is ~ N^1, where N is the number of statistical segments between crosslinks. For an undeformed rubber the mean field is isotropic (15). Under deformation this mean field gives rise to an induced alignment that is also ~ N^1 (11,13,23,24). To this order the two contributions can be separated such that (13)

$$\left\langle P_2(\cos\theta)\right\rangle_{\mathbf{R},V} \approx \left\langle P_2(\cos\theta)\right\rangle_{\mathbf{R}} + \left\langle P_2(\cos\theta)\right\rangle_{V} \qquad \textbf{(4)}$$

where $\langle\cdots\rangle_{\mathbf{R}}$ indicates an averaging over all conformations subject to the limiting imposed by the end to end vector, but without the interactions and $\langle\cdots\rangle_V$ is subject to these interactions, but conversely not to the network vector constraint.

Combining this expression **(4)** for the average orientation with the equation for the transverse relaxation signal **(3)** gives

$$G(t,\lambda) = \mathrm{Re}\left\{\overline{\exp\left[2i\nu_o\left(\left\langle P_2(\cos\theta)\right\rangle_{\mathbf{R}} + \left\langle P_2(\cos\theta)\right\rangle_{V}\right)\right]t}\right\} \qquad \textbf{(5)}$$

A segment of chain in a network is interacting with many neighbouring chains. Therefore the total effect is found by summing over the interactions from these many. These interactions can be well described by an effective mean field (13,15). Furthermore this mean field by its very nature is not unique to any specific network vector, but is common to all segments. The $\overline{(\cdots)}$ indicates an averaging over each network vector, but since $\left\langle P_2(\cos\theta)\right\rangle_V$ will be the same for each segment considered, the NMR response can be simplified to

$$G(t,\lambda) = \mathrm{Re}\left\{\exp\left[2i\nu_o\left\langle P_2(\cos\theta)\right\rangle_V t\right] \times \overline{\exp\left[2i\nu_o\left\langle P_2(\cos\theta)\right\rangle_{\mathbf{R}}\right]t}\right\} \qquad \textbf{(6)}$$

The resultant NMR signal **(6)** is seen to consist of a product of two terms. The first term corresponds to an oscillation, or a splitting, whose frequency depends on the mean field contribution to the average orientation. The second term determines the decay envelope, or lineshape, and is fully specified by the network constraint contribution to the average orientation.

Fourier Transformed Signal

The ability of NMR to separate the two contributions was first mentioned by Sotta (23). Under an affine, uniaxial deformation λ it has been shown that the average orientation of a segment attached to an initial network constraint (X_o, Y_o, Z_o) is given by (11,13)

$$\left\langle P_2(\cos\theta)\right\rangle_{\mathrm{R}} = \frac{1}{2N}\left[\frac{2\lambda^2 Z_o^2 - X_o^2/\lambda - Y_o^2/\lambda}{Nb^2}\right] \qquad \textbf{(7)}$$

where *N* is the number of Gaussian statistical segments of average size *b* between the junction points. If this value is averaged over all the network vectors, this gives the mean orientation due solely to network constraint, $\overline{P_2(\cos\theta)}_{\mathbf{R}}$, as

$$\overline{P_2(\cos\theta)}_{\mathbf{R}} = \frac{1}{3N}\left(\lambda^2 - \frac{1}{\lambda}\right) \qquad \textbf{(8)}$$

The NMR problem requires an integration over all possible network vectors. Each network vector orientation produces a particular frequency of oscillation in the NMR signal, or in Fourier space two Dirac delta functions. The magnitude of this frequency depends on the total contribution from the network constraint and the mean field to the average. It is shown that the NMR spectrum can be determined from

$$G(\nu,\lambda) = \left(\frac{3N\pi}{2\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\left[g_+\left(|\nu| + \frac{\Delta\nu}{2},\lambda\right) + g_-\left(|\nu| - \frac{\Delta\nu}{2},\lambda\right)\right] \qquad \textbf{(9)}$$

where

$$\Delta\nu = 2\frac{\nu_o}{\pi}\left\langle P_2(\cos\theta)\right\rangle_V \qquad \textbf{(9a)}$$

with

$$g_{+}(\nu,\lambda) = \exp\left[-\frac{3N\pi\lambda}{\nu_o}\nu\right] \quad \textbf{(9b)}$$

and when $|\nu| \leq \frac{\Delta\nu}{2}$

$$g_{-}(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right] \quad \textbf{(9c)}$$

or when $|\nu| > \frac{\Delta\nu}{2}$

$$g_{-}(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right]\left\{1 - erf\left[z(\nu)\sqrt{\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)}\right]\right\} \quad \textbf{(9d)}$$

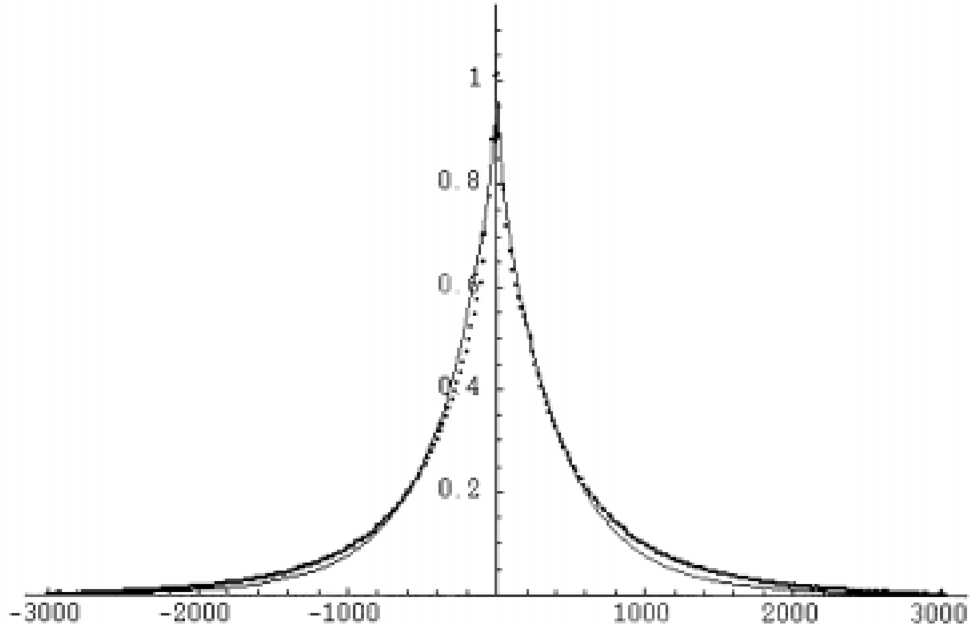
with

$$z(\nu) = \sqrt{\frac{N\pi\nu}{\nu_o}} \quad \textbf{(9e)}$$

In the absence of a mean field contribution to the orientation $\Delta\nu = 0$ this result **(9)** agrees with the theoretical result for a non interacting network. The interacting network result above generates a doublet structure, where the splitting, i.e. the distance in frequency space between the peaks, is given by $\Delta\nu$. It is also important to stress that the splitting does not give the total orientation of the chain segments but merely the contribution from mean field.

Results and discussion

Deuterium nmr has been employed to determine the average orientation of chain segments in the poly(butadiene) networks. The nmr spectrum lineshape reveals the orientational distribution of the network vectors due to the crosslinks, whereas the observed splitting gives information about the orientation due to segmental interactions. Both the lineshape and the splitting has been fitted simultaneously for a range of deformed poly(butadiene) networks. The ^{2}H nmr spectra of the networks under study were analysed in dependence on the deformation ratio λ. As shown in fig. 1 the spectra are well represented by fitting eq. (9) for sample D4 with 0.5 phr DCP at λ=1.0, λ = 1.1 and λ=1.2 (error: ± 0.05).



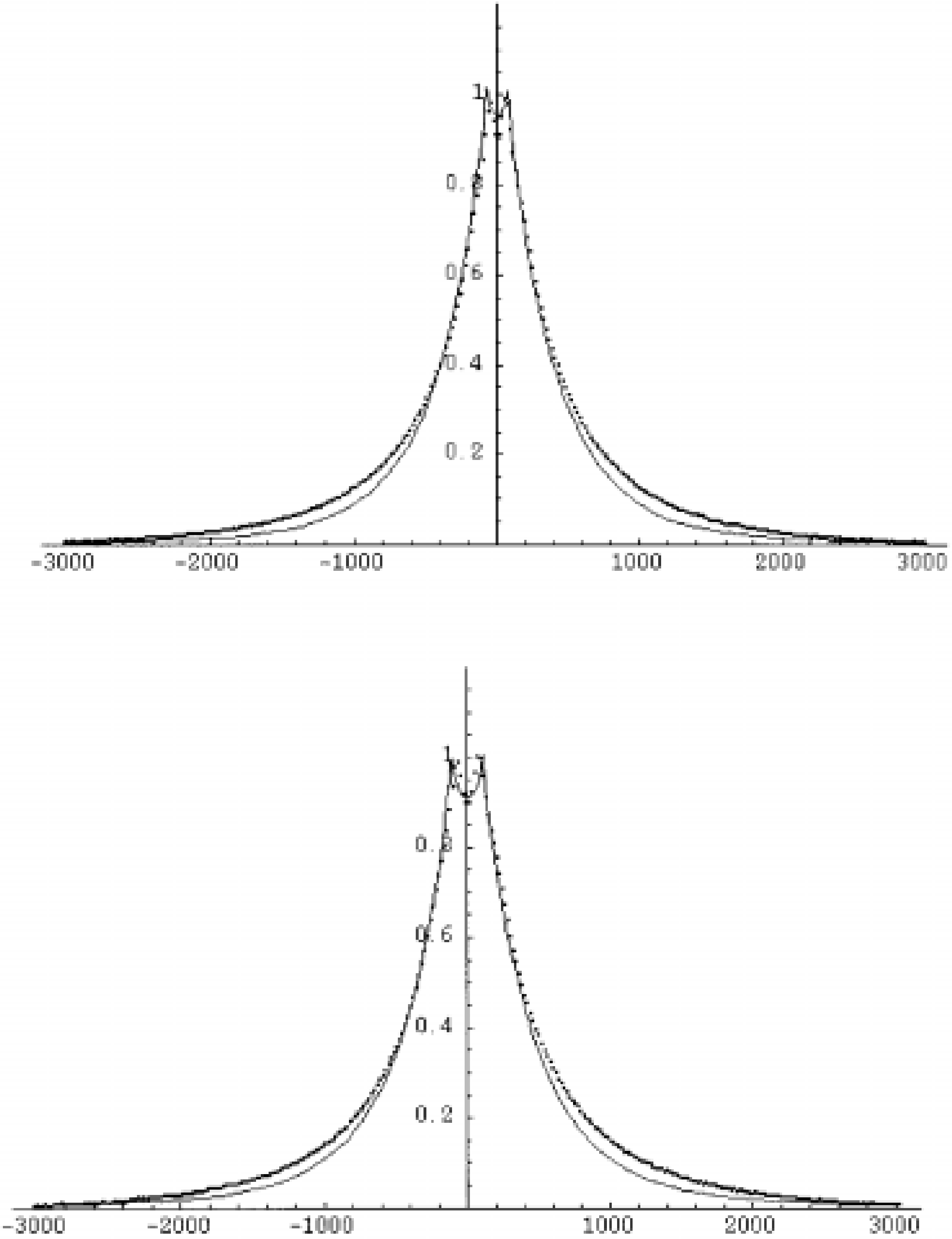


Fig 1: experimental ^{2}H nmr spectra and the fit by eq. **(9)** for sample D4 with 0.5 phr DCP at λ=1.0 (top), λ = 1.1 (middle) and λ=1.2 (bottom)

All the ^{2}H nmr spectra could be described with only three independent parameters: the rescaled quadrupolar interaction divided by the number of statistical segments ν_0/N, the magnitude of splitting in the frequency space $\Delta\nu$ that depends on the mean field contribution to the anisotropy through eq. **(9a)** and the deformation ratio λ. From the fitting parameters the separate contributions to the average orientation of the chain segments arising from the network constraint and from the interactions are calculated. Brereton and Ries (11,13) had shown that the average orientation due to this anisotropic screend potential $\langle P_2(\cos\theta)\rangle_V$ is depending only on the crosslink density and the ratio b/ξ. The latter was found to be unique for all networks under study. It was determined to a value of 3.4 which is as expected in the order of unity and independent on the length of the precursor chains and even on the crosslink density. In a recently published paper the authors (13) already stated as a conclusion that this ratio b/ξ should remain constant for a series with different crosslink densities which was ascertained here. This is a strong indication of the above mentioned theoretical framework.

In the case of peroxide vulcanisation the radicals are created where the peroxide molecules are happen to be located. This implies that there is a risk of local concentrations of radicals, as the peroxide molecules tend to agglomerate rather than dissolve in the polymer matrix. The rate of termination is dependent on the collision frequency which in turn is strongly dependent on the mobility of the system. If the molecular mobility decreases, the polymer chains in which the radicals are located will be less able to move freely to collide with other radicals. Before the radical terminates, it will have time to perform more reactions than a less hindered radical. A lower mobility will, thus, lead to a larger number of crosslinks per initiated radical. However, it is not only the decrease in segmental mobility that is responsible for the increase of crosslink density, even though it is probably the main reason. When the mobility decreases for long-chain segments, the mobility of smaller parts of the chain, e.g. methyl groups in natural rubber or vinyl groups in poly(butadiene), are not affected that much. The vinyl groups therefore are favoured over main chain unsaturations for reactive species, even more pronounced at higher pressures (25). The fact that vinyl unsaturations are prefered in crosslinking was shown already by Lavebrett at al. (26) who investigated butadiene rubber (BR) with different microstructure.

The mean M_C-values between two chemical crosslinks of the networks were estimated from ^1H and ^2H-nmr relaxation, stress-strain and swelling measurements (18) to be 7500 (3300 from swelling only), 3600, 6800 and 5400 g/mol (error: ± 1500 g/mol) for the network D1, D2, D3 and D4. The much larger precursor chain length for D1 and D2 (it is about 2 times larger compared to D3 and D4) yield to a more restricted mobility of the polymer chains. Therefore the resulting crosslink density is increased (reduced M_C-value) for this networks despite of the fact that the inserted amount of crosslinker was the same (about 0.5 phr DCP for all networks under study here). The large discrepancy in the M_C-values calculated from the different methods for the network D1 is probably caused by irregularities in the spatial distribution of the radicals which may give rise to variations in the homogeneity of the resulting network.

The ratio ν_0/N was estimated to be 5200, 5100, 3800 and 3700 Hz for the networks D1, D2, D3 and D4, resp., by fitting the spectra using eq. (9). This trend is in good agreement with the G'-modulus measurements which give plateau values for G' of 1,37 MPa, 1,46 MPa, 1,13 MPa and 1,09 MPa for the same networks. Due to these results the authors believe that the M_C-value for the D1-network of about 3300 g/mol is the more correct one. The networks prepared from larger precursor chains yields the larger ratio ν_0/N than that built from shorter chains, however, they differ by a factor of two in the crosslink density. But if the protonated precursor chain length was the same and the deuterated chain length is larger one could observe only a small increase in this ratio. This ratio ν_0/N in turn is used to determine an effective molecular mass M_{eff} ($1/M_{eff} = 1/M_C + 1/M_{Entanglement}$) which contains the topological hindrances due to crosslinks and entanglements. The value of the corresponding rescaled interaction constant ν_0 for methylene deuterium was taken from an earlier published paper on poly(butadiene) melts (13,27) where it was estimated to be 7730 Hz. In the same study (27) it was found the molecular weight of a nmr statistical segment is (260 ± 30 / 294^*) g/mol. Using this values, the effective molecular masses M_{eff} of these networks were determined to $390/590^*$, $400/604^*$, $530/920^*$ and $540/960^*$ g/mol, resp. (* is upper limit). The entanglement contribution $M_{Entanglement}$ was found to be about 1700 g/mol for the given microstructure (28) (see table 1). Based on this value for $M_{Entanglement}$ and the above summarised mean molar masses between crosslinks M_C estimated from other independent experiments the expected effective molar masses M_{eff} ($1/M_{eff} = 1/M_C + 1/M_{Entanglement}$) were calculated as 1120, 1160, 1360 and 1290 g/mol for the D1, D2, D3 and D4 networks, resp., which is close to the above nmr determined value for the effective molecular weight.

The ability of the theoretical result (13) to measure a crosslink density that compares well with mechanical tests and a screening length of a resonable size of about 0.2 nm which is found to be independent on the precursor chain length and crosslink density, strongly supports the use of this framework to interpret the nmr response from strained elastomers.

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