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Contributions to the Total Orientation of Deformed Elastomers Arising from the Network Structure and Chain Interactions As Measured by NMR

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ABSTRACT: Deuterium NMR has been employed to determine the average orientation $\overline{P_2(\cos\theta)}$ of chain segments in poly(butadiene) networks. It is shown that the free induction decay separates the contribution to the orientation arising from the network constraint to that from chain interactions. The NMR spectrum line shape reveals the orientational distribution of network vectors due to the cross-links, whereas the observed splitting gives information about the orientation due to segmental interactions. Both the line shape and splitting have been fitted simultaneously for a range of deformed poly(butadiene) networks. 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. These in turn are used to determine the molecular weight between cross-links and the size of the segmental interactions, which we choose to express in terms of the Edwards' screening length. This work is also important to computer modeling of the stress−optical coefficient where the interchain interactions are ignored.

I. Introduction

Macroscopic strain applied to elastomeric networks induces orientation in the constituent polymer chains. Nuclear magnetic resonance (NMR) is used to the study the anisotropy at a molecular level in elastomers.[1−5] The important feature considered in this work is the contribution to the total orientation coming from interchain interactions in the deformed rubber.

The usual approach has been to consider a single chain whose orientation arises only from the constraint of the cross-links on its end-to-end vector. In this paper, we will show that interchain interactions, which we will assume to be isotropic in the undeformed state, can become anisotropic in the deformed state and thereby significantly contribute to the total orientation of the chains. Furthermore we will demonstrate that from a measurement of the free induction decay we are able to separate unambiguously the two contributions to the orientation.

For an undeformed rubber, a single resonance line in the deuterium NMR spectrum is observed.[6] Under uniaxial deformation, the spectrum splits into a well-defined doublet structure corresponding to an oscillation in the free induction decay.[7] We will show that the usual network constraint on the end-to-end vector determines the line shape under deformation, while the interactions lead to the splitting.

It is known that a noninteracting Gaussian network shows no splitting under deformation.[8] This indicates that, to account for the NMR splitting, one must introduce segmental interactions.[9] Several explanations have been put forward to account for the splitting observed from strained deuterated networks, these include the following: nematic interactions,[10] excluded volume interactions,[11] and anisotropic junction fluctuations.[12] An analytic result will be derived that includes the effect of network constraints and chain interactions.

It is shown from analyzing free induction decays from a range of deformed network samples that, for small deformations, the assumption of initially Gaussian distributed network vectors that then undergo affine deformation adequately describes the NMR response. The NMR interaction term, the static quadrupolar constant, is effectively reduced in magnitude by rapid local level reorientations subject to both the constraint from the monomer being attached between cross-links and the interactions of the segments with their environment.

In a network a polymer segment interacts with many neighboring ones. These many interactions can be described by an effective mean field.[13,14] In an NMR spectrum the distance between the doublets in frequency space is determined by the mean field, whereas the line shape is given by the network vector distribution. NMR is thus able to monitor the average orientation due to the cross-links and the mean field separately, allowing the two contributions to the total average orientation $\overline{P_2(\cos\theta)}$ to be evaluated.

A theoretical interpretation by Brereton and Ries[11] attributes the higher degree of anisotropy implied by the splitting to excluded volume interactions within the rubber. Under deformation the distribution of monomeric units generate, through their excluded volume interactions, an anisotropic mean field. All chains and even solvent molecules within the rubber matrix experience this mean field that causes an induced alignment along the strain direction.[15−18] The resultant splitting is found to be dependent on the size of the excluded volume interaction.[11]

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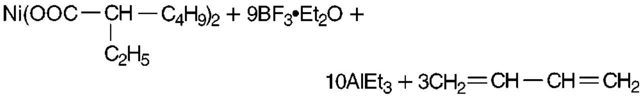
This work builds on an earlier NMR study that analyzed a range of linear poly(butadiene) melts.[19] In that work, the deuterium transverse relaxation was investigated to determine the size of a statistical segment and the magnitude of its corresponding rescaled quadrupolar coupling constant ν_0. Rapid internal conformational changes within a single statistical segment reduce the magnitude of the static quadrupolar coupling constant, giving rise to a rescaled value. These two parameters found in the previous study of well-characterized monodisperse linear chains are required in analyzing the spectra from strained deuterated networks.

II. Experimental Section

All NMR experiments were carried out at room temperature on a Varian Unity 400 wide bore spectrometer (400 MHz proton frequency) operating at 61.3 MHz for deuterons. Spectra were obtained using a standard 90 radio frequency pulse of approximate 7 μs. The deuteron measurements under mechanical deformation were performed by a simple stretching device parallel to the static magnetic field B_o. The stretching ratio was determined from the distance between two marks on the sample, before and after stretching. Typically the sample size was 3.5 cm long, 0.5 cm wide, and 1.5 mm thick.

The partially deuterated poly(butadiene) was polymerized on the basis of (1,1,4,4-d_4)-butadiene (Promochem 98%, stabilized by Hydrochinon) by a conventional (commercially used) Ziegler−Natta catalyst. The result is a methylene-labeled high-1,4-*cis*-poly(butadiene) (98% cis microstructure). Toluene (Aldrich, 99.8%) was used as solvent. 2,4-Di-*tert*-butyl-*p*-cresol was added for aging protection.

The following is the composition of the catalyst:



$$Ni(OOC{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}{-}C_4H_9)_2 + 9BF_3{\bullet}Et_2O + 10AlEt_3 + 3CH_2{=}CH{-}CH{=}CH_2$$

The microstructure was determined by ^{13}C NMR and showed a 98% cis microstructure. Molecular weights were determined by GPC: M_n(D)= 25 000 and M_w(D) = 120 000 and a wide molar mass distribution (U = 3.75). This polymer was mixed in a ratio of 1:9 with the nearly corresponding commercial nondeuterated poly(butadiene) BUNA cis 132 M_n(H) = 19 000, M_w(H) = 70000, U = 3.68). 1 phr dicumyl peroxide (DCP) was used as the cross-linking agent for all networks prepared. The samples were vulcanized in a vulcameter press at 145 °C and 100 bar for 1 h. The resulting mean molar mass between two chemical cross-links, M_c, determined from mechanical stress−strain measurements[20] is about 6500 g/mol for all the samples.

III. Theory

Introduction. A scale invariant model consisting of a series of statistical units $\{\mathbf{b}_j\}$ is used to model the NMR properties of the network chains. As introduced by Cohen-Addad[21,22] and further developed by Brereton[23,24] the carbon−deuterium quadrupolar interaction is rescaled by rapid local reorientations onto this coarse-grained representative chain.

In the regime where the local level bond dynamics are fast compared to the time scale set by the rescaled quadrupolar interaction, ν_0, the relaxation of the transverse components of the magnetization can be written as[28]

$$G(t,\lambda) = \exp\left(-\frac{t}{T_2}\right)\overline{\cos[2\nu_0\langle P_2(\cos\theta)\rangle t]} \tag{1}$$

where θ is the angle the applied magnetic field makes with the statistical segment $\mathbf{b}_j$ and $P_2(\cdots)$ is the second-order Legendre polynomial. The $\langle\cdots\rangle$ is an annealed average over all the available conformations subject to the network constraint imposed by the deformation λ through the cross-links, while the $\overline{(\cdots)}$ indicates a quenched average over all cross-link points. The T_2 term corresponds to the intrinsic line width of the poly(butadiene) sample and is related to the fluctuating part of the NMR Hamiltonian.[28] At temperatures sufficiently above T_g in a network this contribution evolves much slower than the cosine term. In an earlier study on poly(butadiene) we measured T_2s from a range of linear uncross-linked samples, giving a measure of the intrinsic line width term.[19] The network samples decay on a time scale that is approximately 20 times shorter than linear chains of a corresponding molecular weight to that of the cross-link density. This reveals that this broadening can be neglected with very little loss in accuracy, i.e., we can write[11]

$$G(t,\lambda) = \overline{\cos[2\nu_0\langle P_2(\cos\theta)\rangle t]} \tag{2}$$

An Interacting Network. The important point in this work is that there are two principal factors that influence the averaging over all the available conformations of the NMR active bond. First, there is the constraint caused by the junction points. The end-to-end vector formed by two consecutive cross-links determines a static residual average orientation of the labeled bond. Second, there are the interactions of the chain segments in the rubber with their many neighbors. 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.

The network constraint $\mathbf{R}$ and the interactions V will contribute to the average orientation of the chains. The orientation due to the network constraint in the absence of any interactions is $\sim N^{-1}$,[27] where N is the number of statistical segments between cross-links. The interchain interactions V collectively form a mean field, which in an undeformed rubber is isotropic[14] and therefore does not contribute to the orientation. However, in the deformed rubber, the mean field becomes anisotropic and makes a contribution. The effect of the mean field on a single chain is expressed as a deformation dependent screened potential $V^*(\lambda)$.[11] Only the anisotropic part will contribute to the orientation and its effect, through the Boltzmann factor, can be treated as a perturbation, i.e.

$$\exp\left[\frac{V^*(\lambda)}{kT}\right] \approx 1 + \frac{V^*(\lambda)}{kT} + ...$$

In our earlier work[11] we showed that the effect of $V^*(\lambda)$ in the deformed state was also the same as $\sim 1/N$, justifying our perturbative approach. Hence to this order we can write[25,26]

$$\langle P_2(\cos\theta)\rangle_{\mathbf{R},V} \approx \langle P_2(\cos\theta)\rangle_{\mathbf{R}} + \langle P_2(\cos\theta)\rangle_V \tag{3}$$

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. In this way the effect of the constraint and the interchain interactions are additive.[11]

Combining this expression (eq 3) for the average orientation with the equation for the transverse relaxation signal (eq 2) gives

$$G(t,\lambda) = \mathrm{Re}\{\overline{\exp[2i\nu_o(\langle P_2(\cos\theta)\rangle_{\mathbf{R}} + \langle P_2(\cos\theta)\rangle_V)]t}\} \tag{4}$$

It is possible to see the effect of including the extra term $\langle P_2(\cos\theta)\rangle_V$ on the transverse relaxation, without as yet going into the details of the mathematics. A segment of chain in a network is interacting with many neighboring chains. The total effect is found by summing over the interactions from these many chains, with this then naturally self-averaging the interactions. These interactions can therefore be well described by an effective mean field.[14] 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 $\langle P_2(\cos\theta)\rangle_V$ will be the same for each segment considered, it can come out from under the $\overline{(\cdots)}$. This means the NMR response can be written as

$$G(t,\lambda) = \mathrm{Re}\{\exp[2i\nu_o(\langle P_2(\cos\theta)\rangle_V t] \times \overline{\exp[2i\nu_o(\langle P_2(\cos\theta)\rangle_{\mathbf{R}} t]}\} \tag{5}$$

The important point is that the resultant NMR signal (eq 5) is seen to consist of a product of two terms. The first term corresponds to an oscillation in the free induction decay, or a splitting in the Fourier spectrum, whose frequency depends on the mean field contribution to the average orientation. The second term determines the decay envelope, or line shape, 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 et al.[25] What follows here is a new analytic result for the NMR Fourier transformed spectrum of eq 5. This expression will then be compared to a range of experimental data, enabling NMR to be a probe of the mean field and cross-link density. The NMR spectrum in frequency space ν, $G(\nu,\lambda)$, can be derived from

$$G(\nu,\lambda) = \int e^{2\pi i\nu t} G(t,\lambda)\,\mathrm{d}t \tag{6}$$

Before this calculation is made, a form is needed for the averaging over all network vectors, $\overline{(\cdots)}$, in eq 5 and a relationship between the network end-to-end vector and the average orientation of a subsequent segment. In this work it will be assumed that the initial Cartesian components of the network end-to-end vectors, $\{X_0, Y_0, Z_0\}$, are Gaussian-distributed and that these then undergo uniaxial affine deformation. This means that the averaging $\overline{(\cdots)}$ denotes an integration over a probability distribution, i.e.

$$\overline{(\cdots)} = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} (\cdots) \exp\left[\frac{-3(X_0^{\,2} + Y_0^{\,2} + Z_0^{\,2})}{2Nb^2}\right] \mathrm{d}X_0 Y_0 Z_0 \tag{7}$$

Under an affine, uniaxial deformation λ it can be shown that the average orientation of a segment attached to an initial network constraint (X_0, Y_0, Z_0) is given by[11]

$$\langle P_2(\cos\theta)\rangle_{\mathbf{R}} = \frac{1}{2N}\left[\frac{2\lambda^2 Z_0^{\,2} - X_0^{\,2}/\lambda - Y_0^{\,2}/\lambda}{Nb^2}\right] \tag{8}$$

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, using the above averaging equation, eq 7, this gives the mean orientation due solely to network constraint, $\overline{P_2(\cos\theta)_{\mathbf{R}}}$, as

$$\overline{P_2(\cos\theta)_{\mathbf{R}}} = \frac{1}{3N}\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{9}$$

which is different from the result for a system of rigid rods where it is found that[27]

$$\overline{P_2(\cos\theta)_{\mathbf{R}}} = \frac{1}{5N}\left(\lambda^2 - \frac{1}{\lambda}\right)$$

The NMR problem posed by eqs 5–8 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 δ functions. The magnitude of this frequency depends on the total contribution from the network constraint and the mean field to the average orientation; recall eq 4. The summation over all network chains, giving the resultant theoretical spectrum $G(\nu,\lambda)$ is derived in the Appendix. There it is shown that the NMR spectrum can be determined from

$$G(\nu,\lambda) = \left(\frac{3N\pi}{2\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\left[g_+\left(\left|\nu\right| + \frac{\Delta\nu}{2},\lambda\right) + g_-\left(\left|\nu\right| - \frac{\Delta\nu}{2},\lambda\right)\right] \tag{10}$$

where

$$\Delta\nu = 2\frac{\nu_o}{\pi}\langle P_2(\cos\theta)\rangle_V \tag{10a}$$

with

$$g_+(\nu,\lambda) = \exp\left[-\frac{3N\pi\lambda}{\nu_o}\nu\right] \tag{10b}$$

and when $|\nu| \le \Delta\nu/2$

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right] \tag{10c}$$

or when $|\nu| > \Delta\nu/2$

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right]\left\{1 - \mathrm{erf}\left[z(\nu)\sqrt{\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)}\right]\right\} \tag{10d}$$

with

$$z(\nu) = \sqrt{\frac{\mathrm{N}\pi\nu}{\nu_o}} \tag{10e}$$

Parts b and d of eq 10 correct a minor numerical error in the result of eq 3.8 in ref 8, which has also been noted elsewhere.[9] However eq 10 represents a substantial

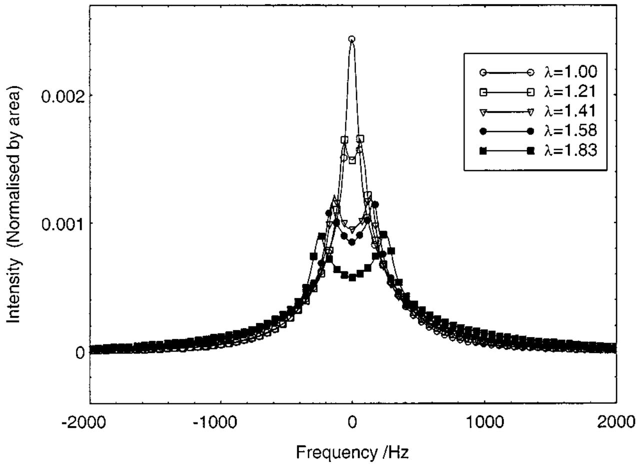


Figure 1. Range of NMR spectra from a strained poly(butadiene) network, where λ is the deformation ratio. The solid lines are to guide the eye.

correction to the result (eq 5.2) in ref 8, although both expressions give qualitatively similar results.

In the absence of a mean field contribution to the orientation $\Delta\nu = 0$ this result (eq 10) agrees with the theoretical result for a noninteracting network. The calculation of the Fourier-transformed phantom network signal can be found in the literature and has been the concern of a recent paper by Warner et al.[9] An important point to note is that the noninteracting network does not generate the oscillation that is seen in experimental data. In contrast, 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 consequently does not give the total orientation of the chain segments but merely the contribution from the mean field. In this way NMR can decouple the resultant orientation due to the chain interactions from that of the network constraint. This is the main result of this study.

IV. Results and Analysis

The NMR spectra for a range of deformations from a poly(butadiene) network have been recorded. The signal intensities have been normalized so as to have a unit area under each spectrum, with these displayed in Figure 1.

The aim of the subsequent work is to quantify the two contributions to the average orientation of the polymer segments. To achieve this, eq 10 will be employed to interpret the NMR frequency response of the deformed networks. This expression has three independent parameters: the rescaled interaction constant divided by the number of statistical segments between cross-links ν_0/N, the magnitude of splitting in frequency space $\Delta\nu$ that depends on the mean field contribution to the anisotropy through eq 10a, and the deformation λ. An Excel program has been written to fit the theoretical spectrum (eq 10) to the data, by minimizing the root-mean-square difference between the theoretical line shapes and the data recorded.

There is a ~5% experimental error in determining λ, so the fitting procedure allows for small changes in the required theoretical deformation ratios. As we are examining the same network at each λ, ν_0/N must be the same for each theoretical spectrum, therefore this will be treated as a global fitting parameter. Essentially only $\langle P_2(\cos\theta)\rangle_V$ is allowed to vary between data sets.

Table 1. Parameters Required in the Theoretical NMR Signal (10) To Model the Data in Figure 2

exptl λ	fitting λ	$\overline{P_2(\cos\theta)}_{\mathbf{R}}$	$\langle P_2(\cos\theta)\rangle_V$	$\langle P_2(\cos\theta)\rangle_V/\overline{P_2(\cos\theta)}_{\mathbf{R}}$
1.00	1.00	0	0	
1.21	1.29	0.086	0.024	0.28
1.41	1.49	0.15	0.055	0.37
1.58	1.56	0.17	0.063	0.37
1.83	1.83	0.27	0.10	0.38
ν_o/N (Hz)	2200 ± 200			
M_x	900 ± 200			

In an earlier study[19] on poly(butadiene) it was found the molecular weight of a NMR statistical segment is 260 ± 30 and the corresponding rescaled interaction constant for the methylene deuterium is $\nu_0 = 7730$ Hz. From these values and the ν_0/N required to fit the data, it is simple to determine N and thus the actual molecular weight between cross-links and the mean orientation $\overline{P_2(\cos\theta)}_{\mathbf{R}}$ due to the network constraint from eq 9. The fitting parameters can be found in Table 1 and the corresponding theoretical spectra are compared to the data in Figure 2.

From Table 1 it can be seen that the theoretically required deformation ratios are close to the experimentally determined ones and indeed are within the ~5% estimated error in λ. This means that NMR was able to measure the deformation of the samples from the NMR Fourier transformed signals. It is only at the highest deformation, $\lambda = 1.83$, that the theoretical line shape deviates from the experimental data. This could be attributed for example to nonaffine deformation of the effective cross-link points at high elongations.

Stress strain measurements[20] on this network have determined the molecular weight between chemical cross-links, M_c, as 6500 and the molecular weight between entanglements, M_e, as 1970. The effective molecular weight between cross-links, M_x, can be estimated from[28]

$$\frac{1}{M_x} = \frac{1}{M_e} + \frac{1}{M_c} \tag{11}$$

This gives a value of $M_x = 1500$, which is close to the above NMR-determined value in Table 1. Through the new analytic result (eq 10), it is therefore possible to measure the average molecular weight between effective cross-link points.

In Table 1, the relative contribution to the orientation of the mean field to the network constraint has been determined. The mean field appears to increase the alignment, in terms of a resultant $\langle P_2(\cos\theta)\rangle_{\mathbf{R},V}$, by approximately 35%. The remaining part of the analysis section shall consider a proposed model for this anisotropic mean field.

Edwards' Screening Length. A segment in a polymer melt interacts through excluded volume interactions with its many neighboring chains. These many interactions of the segment with its environment give rise to an effective interaction potential between any two segments on a particular chain, $V^*(\mathbf{r})$, given by[14]

$$V^*(\mathbf{r}) = V\left[\delta(\mathbf{r}) - \frac{\exp(-r/\xi)}{4\pi r\xi^2}\right] \tag{12}$$

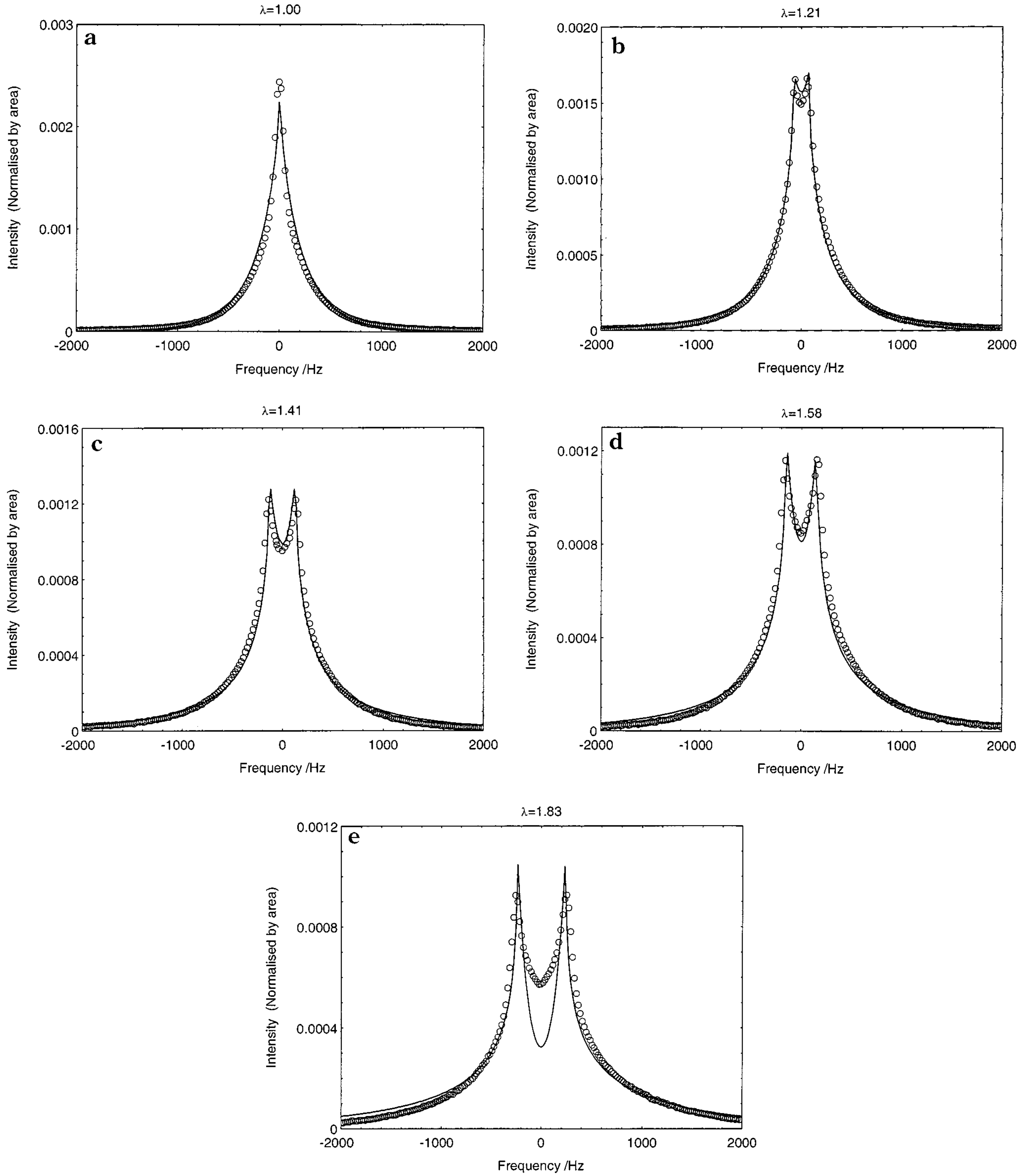


Figure 2. Solid lines showing the theoretical fits from eq 10 to strained poly(butadiene) network using the parameters in Table 1. λ is the deformation ratio. (a) $\lambda = 1.00$. (b) $\lambda = 1.21$. (c) $\lambda = 1.41$. (d) $\lambda = 1.58$. (e) $\lambda = 1.83$.

where V is the bare excluded volume interaction strength, ξ is the Edwards' screening length, and $\mathbf{r}$ is the vector separating the two segments. This potential consists of the strong repulsive short-range excluded volume component, $\delta(\mathbf{r})$, and a weak attractive part of range ξ. The Edwards' screening length is related to V through[11]

$$\xi = b\sqrt{\frac{kT}{12Vc}} \tag{13}$$

where c is the number of statistical segments per unit volume and k is the Boltzmann constant.

From eq 12, the effective interaction potential satisfies $\int V^*(\mathbf{r})\, \mathrm{d}\mathbf{r} = 0$.[14] This effect is known as the screening of the excluded volume interactions. In an undeformed melt, it is this screening that gives rise to Gaussian statistics, rather than self-avoiding walk statistics.

The Fourier transform components $V_q{}^*$ of the screened interaction potential (eq 12) can be written in terms of

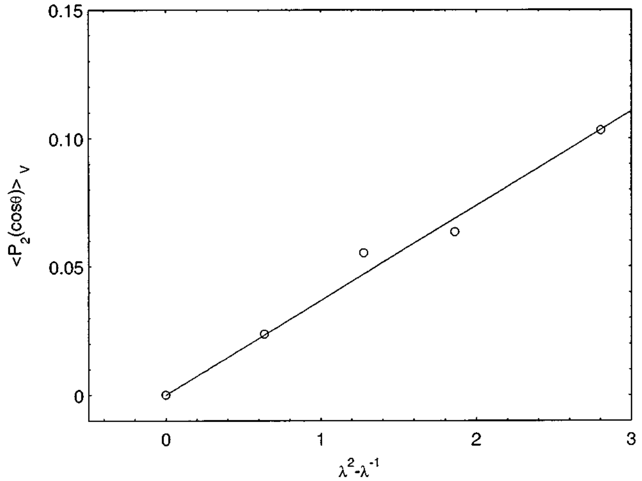


Figure 3. Average orientation due to the contribution from the mean field $\langle P_2(\cos\theta)\rangle_V$ as a function of $\lambda^2 - \lambda^{-1}$.

the components of the bare interaction V_q as[14]

$$V_q^* = V_q - \frac{V_q^{\,2} g_q}{1 + V_q g_q} \tag{14}$$

where in the case of a network g_q becomes the sum of the structure factors of the network chains divided by the number of network chains.[11,29-31] These network chain structure factors then depend on the deformation λ. It is through this dependence of the structure factors on elongation that the interaction potential itself becomes anisotropic.

In a paper by Brereton and Ries the average orientation due to this anisotropic screened potential was calculated to be[11]

$$\langle P_2(\cos\theta)\rangle_V = \frac{1}{15N\pi}\frac{b}{\xi}\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{15}$$

with this depending on the cross-link density and the ratio of the length scales b/ξ.

In Figure 3 the orientation due to the mean field is plotted as a function of ($\lambda^2 - \lambda^{-1}$). As we know the molecular weight between cross-links, N, a straight line fit to the data in Figure 3 specifies the ratio of the screening length to the average statistical segment size. This gives $b/\xi = 6.0 \pm 0.6$, which as expected is the on the order of unity.[32]

If this model of excluded volume interactions for the mean field had been adopted earlier in the analysis, as opposed to having taken the more general approach, it would have been possible to fit all the NMR signals simultaneously using only two parameters; $\nu_o/N = 2200$ Hz and $\xi = b/6.0$. This is a strong indication of the above theoretical framework to model correctly the NMR response.

From the characteristic ratio C_∞ an absolute value of the screening length can be estimated. This ratio gives the average end to end distance $\langle \mathbf{R}^2\rangle$ for a chain comprising N' atomic bonds of length l_i through the expression[33]

$$C_\infty = \frac{\langle \mathbf{R}^2\rangle}{\sum_{i=1}^{N'} l_i^{\,2}} \tag{16}$$

For poly(butadiene) both the cis and trans forms have a characteristic ratio near 5.[34] From this the average end-to-end distance of the statistical segment, b, of molecular weight 260 ± 30 can be calculated as approximately 15 Å. The ratio $\xi = b/6.0$ gives an Edwards screening length, therefore, of 2.5 Å. At distances greater than that, on the order of a bond length, the excluded volume interactions are therefore screened. This is a reasonable length scale for screening and supports the notion that excluded volume interactions are sufficient to account for the observed splitting seen in NMR spectra from strained networks.

V. Conclusions

NMR has been used to measure the orientation of chain segments within deformed poly(butadiene) networks. An analytic result was derived that takes into account two contributions to the total orientation of the constituent polymer chains. It was found that the free induction decay readily separates the effect of chain interactions with their environment from that of the network constraint, i.e., the presence of cross-links within the rubber matrix, on the polymer segmental anisotropy. This makes NMR a useful complementary tool to techniques such a birefringence that measure the total average orientation.

The theoretical NMR relaxation function from a strained network was found to consist of an oscillation within a decay envelope. The oscillation is related to the anisotropy stemming from the interactions of the chains with their environment. This interaction of a monomer with its many surrounding segments can be described by an effective mean field.[14] Under deformation this mean field becomes anisotropic in nature.[11] The frequency of the oscillations in the signal is directly related to the magnitude of the induced orientation from this mean field through eq 10a. Therefore the splitting in frequency space is indicative of chain interactions. In contrast, the decay envelope is specified by the distribution of network vectors in the rubber.

The analytic result for the NMR response of a strained network was compared to experimental data from a range of deformed poly(butadiene) rubbers. It was found that the theoretical decay modeled the data well, until the deformation became too large, $\lambda \sim 2$. Here assumptions such as the affine deformation of effective cross-link points are expected to break down.[35]

The theoretical decay envelope is fully specified by the cross-link density through eq 10. A value of ~1000 was required to fit the experimental signals, with this comparing well with the mechanical tests on the same sample.[20] This analytic result therefore allows NMR to monitor the cross-link density.

It was found that the contribution to the orientation from the mean field corresponded to a ~35% perturbation from the noninteracting case. Brereton and Ries[11] have attributed this anisotropic mean field to the excluded volume interactions between chain segments. The contribution from this mean field was expressed in terms of an Edwards' screening length via eq 15. By comparing the λ dependence of this contribution with their theoretical predictions, Figure 3, it was possible to determine an Edwards screening length of 2.5 Å. This indicates that at distances greater than one or two bond lengths the excluded volume interactions are screened.

The ability of the theoretical NMR result to measure a cross-link density that compares well with mechanical tests and a screening length of a reasonable size strongly supports the use of this framework to interpret the NMR response from strained elastomers.

Appendix: Spectrum from a Strained Network with an Added Orientation Due to a Mean Field

The aim of this section is to calculate the NMR spectrum, $G(\nu,\lambda)$, from a strained polymer network. From eqs 4, 6, and 7, we have

$$G(\nu,\lambda) = {}^{1}/_{2}(G_{+} + G_{-}) \qquad \text{(A1)}$$

with

$$G_{\pm} = \int P(\mathbf{R})\left\{\delta\left[\nu \pm \frac{\nu_o}{\pi}(\langle P_2(\cos\theta)\rangle_{\mathbf{R}} + \langle P_2(\cos\theta)\rangle_V)\right]\right\} \mathrm{d}\mathbf{R} \qquad \text{(A2)}$$

and

$$\int P(\mathbf{R})\,\mathrm{d}\mathbf{R} = \left(\frac{3}{2\pi N b^2}\right)^{3/2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\left[\frac{-3({X_0}^2 + {Y_0}^2 + {Z_0}^2)}{2Nb^2}\right]\mathrm{d}X_0Y_0Z_0 \qquad \text{(A3)}$$

where $\{X_0, Y_0, Z_0\}$ are the undeformed Cartesian coordinates of an end-to-end network vector.

The average orientation due only to the network constraint on a statistical segment in a chain comprising N units is given by[11]

$$\langle P_2(\cos\theta)\rangle_{\mathbf{R}} = \frac{1}{2N}\left[\frac{2\lambda^2{Z_0}^2 - {X_0}^2/\lambda - {Y_0}^2/\lambda}{Nb^2}\right] \qquad \text{(A4)}$$

For compactness we define a term $\Delta\nu$ such that

$$\Delta\nu = 2\frac{\nu_o}{\pi}\langle P_2(\cos\theta)\rangle_V \qquad \text{(A5)}$$

The NMR spectrum (eq A1) combined with eqs A2–A5 can be expressed in terms of scaled cylindrical coordinates

$$r^2 = \frac{{X_0}^2 + {Y_0}^2}{\lambda N b^2}, \quad z^2 = \frac{\lambda^2 {Z_0}^2}{Nb^2} \qquad \text{(A6)}$$

as

$$G(\nu,\lambda) = {}^{1}/_{2}[I_{+}(\nu,\lambda) + I_{-}(\nu,\lambda)] \qquad \text{(A7)}$$

where

$$I_{\pm}(\nu,\lambda) = \left(\frac{3}{2}\right)^{3/2}\frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty}\mathrm{d}z\int_0^{\infty}\mathrm{d}r^2\,\exp\left[-\frac{3}{2}\left(\lambda r^2 + \frac{z^2}{\lambda^2}\right)\right]\delta\left\{\nu \pm \left[\frac{\nu_o}{\pi}\frac{1}{2N}(2z^2 - r^2) + \frac{\Delta\nu}{2}\right]\right\} \qquad \text{(A8)}$$

The two integrals $I_{+}(\nu,\lambda)$ and $I_{-}(\nu,\lambda)$ must be evaluated separately. The following analysis will only consider $\nu/\nu_o \geq 0$, as the signal must be symmetric. It will also be assumed that $\Delta\nu \geq 0$, which implies that the induced orientation due to the mean field is in the same direction as the strain.

For $I_{+}(\nu,\lambda)$ the integrand is zero unless $r^2 = 2[N\pi(\nu + \Delta\nu/2)/\nu_o + z^2]$. Since r^2 will remain positive for all z, $\nu/\nu_o \geq 0$, and $\Delta\nu \geq 0$, the remaining integral over z is unrestricted. From the property of a δ function we have

$$I_{+}(\nu,\lambda) = \left(\frac{2N\pi}{\nu_o}\right)\left(\frac{3}{2}\right)^{3/2}\frac{1}{\sqrt{\pi}}\exp\left[-\frac{3\pi N\lambda}{\nu_o}\left(\nu + \frac{\Delta\nu}{2}\right)\right]\int_{-\infty}^{+\infty}\mathrm{d}z\,\exp\left[-\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)z^2\right] \qquad \text{(A9)}$$

This is now in the form of a standard Gaussian integral, so

$$I_{+}(\nu,\lambda) = \left(\frac{3N\pi}{\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\exp\left[-\frac{3N\pi\lambda}{\nu_o}\left(\nu + \frac{\Delta\nu}{2}\right)\right] \qquad \text{(A10)}$$

For the $I_{-}(\nu,\lambda)$ the integrand is zero unless $r^2 = 2[-N\pi(\nu - \Delta\nu/2)/\nu_o + z^2]$. The integration over the variable z must be constrained so as to keep $r^2 \geq 0$. This then defines two intervals over which $I_{-}(\nu,\lambda)$ should be considered.

In the range $\nu \leq \Delta\nu/2$, the variable z is unrestricted as $r^2 \geq 0$. In this region, we have

$$I_{-}(\nu,\lambda) = \left(\frac{2\pi N}{\nu_o}\right)\left(\frac{3}{2}\right)^{3/2}\frac{1}{\sqrt{\pi}}\exp\left[\frac{3N\pi\lambda}{\nu_o}\left(\nu - \frac{\Delta\nu}{2}\right)\right]\int_{-\infty}^{+\infty}\mathrm{d}z\,\exp\left[-\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)z^2\right] \qquad \text{(A11)}$$

The integral is again in a standard Gaussian form, giving

$$I_{-}(\nu,\lambda) = \left(\frac{3N\pi}{\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\exp\left[\frac{3N\pi\lambda}{\nu_o}\left(\nu - \frac{\Delta\nu}{2}\right)\right] \qquad \text{(A12)}$$

In the second region, $\nu > \Delta\nu/2$, the variable z must be constrained so as to keep $r^2 \geq 0$. Thus for a nonzero integrand $|z| > z(\nu - \Delta\nu/2) = \sqrt{N\pi(\nu - \Delta\nu/2)/\nu_o}$, giving

$$I_{-}(\nu,\lambda) = \left(\frac{2N\pi}{\nu_o}\right)\left(\frac{3}{2}\right)^{3/2}\frac{1}{\sqrt{\pi}}\exp\left[\frac{3N\pi\lambda}{\nu_o}\left(\nu - \frac{\Delta\nu}{2}\right)\right]2\int_{z(\nu-\Delta\nu/2)}^{+\infty}\mathrm{d}z\,\exp\left[-\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)z^2\right] \qquad \text{(A13)}$$

The integral can then be written in terms of the error function erf(···) as

$$I_{-}(\nu,\lambda) = \left(\frac{3N\pi}{\nu_o}\right)\left(2\lambda + \frac{1}{\lambda^2}\right)^{-1/2}\exp\left[\frac{3N\pi\lambda}{\nu_o}\left(\nu - \frac{\Delta\nu}{2}\right)\right]\left\{1 - \mathrm{erf}\left[z\left(\nu - \frac{\Delta\nu}{2}\right)\sqrt{\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)}\right]\right\} \qquad \text{(A14)}$$

The resultant spectrum must be symmetric about $\nu = 0$, so it can be written from the above analysis as

$$G(\nu,\lambda) = \left(\frac{3N\pi}{2\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\left[g_{+}\left(|\nu| + \frac{\Delta\nu}{2},\lambda\right) + g_{-}\left(|\nu| - \frac{\Delta\nu}{2},\lambda\right)\right] \qquad \text{(A15)}$$

where

$$\Delta\nu = 2\frac{\nu_o}{\pi}\langle P_2(\cos\theta)\rangle_V \qquad \text{(A16)}$$

with

$$g_+(\nu,\lambda) = \exp\left[-\frac{3N\pi\lambda}{\nu_o}\nu\right] \tag{A17}$$

and when $|\nu| \leq \Delta\nu/2$

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right] \tag{A18}$$

or when $|\nu| > \Delta\nu/2$

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_o}\nu\right]\left\{1 - \operatorname{erf}\left[z(\nu)\sqrt{\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)}\right]\right\} \tag{A19}$$

with

$$z(\nu) = \sqrt{\frac{N\pi\nu}{\nu_o}} \tag{A20}$$

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