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Susceptibility Effect of Carbon Black Filler on the Deuterium NMR Line Shape from Poly(butadiene) Networks

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ABSTRACT: Deuterium NMR line shapes of carbon black (N220) filled *cis*-1,4-poly(butadiene) networks have been examined. The effect of the susceptibility of the filler on the NMR line shape has been considered. The theory proposed by Brereton and Ries for deuterium NMR line splitting in spectra of polymer networks was used to fit the experimental data. It was found that the polymer segments near the surface of a filler particle experience a different local magnetic field from the remaining segments, due to the susceptibility of the carbon black. This effect gives rise to an asymmetry in the NMR spectrum, which until now has not been explained. Additionally, this analysis determines the fraction of polymer units affected by the local field of the filler particles and provides information about the effect of the macroscopic deformation on these attached chains.

Introduction

The aim of this paper is to explain the asymmetric NMR spectra observed from deformed carbon black filled poly(butadiene) networks.[1] To illustrate this asymmetry, we show in Figure 1 a comparison between a NMR spectrum from a filled and unfilled strained network. We consider the effect of the susceptibility of the carbon black filler on the local field of polymer chains that are in the vicinity of these particles. We propose that the magnetic field near carbon black particles is different from the rest of the sample. Therefore, the polymer chains close to the filler particles experience a different resonance frequency. This change in frequency causes a shift of their NMR spectrum in the Fourier transformed signal relative to the unbound segments. To quantify this shift, we employed the theoretical expression of Brereton and Ries to model the NMR line shape and splitting.[2] We then calculated the expected shift in frequency by using susceptibility data[3] of carbon black and show that this compares favorably with the results obtained from our fitting procedure.

As well as the susceptibility of the carbon black filler, we also consider that the applied macroscopic deformation does not affect the chains closely attached to filler particles to the same degree as it does the remaining chains. Figure 2 shows schematically the various possibilities of polymer chain attachments to the filler particles.[4] Chain segments E, F, and D are not affected directly by the macroscopic deformation.

Our approach is to consider the asymmetric spectrum as consisting of two main components. The first corresponds to the NMR signal of polymer chains that are far away from the filler particles. These chains have a spectrum that is essentially identical to that of an unfilled network. The second is the spectrum from the polymer chains that are very close to the filler particles such as segments E in Figure 2. The carbon black causes a shift in the resonance frequency and a different bulk strain orientation dependence of these chains attached to the filler particles. The two components of the resultant NMR line shape are schematically shown in Figure 3a,b. What we experimentally observe from the filled polymer network is the collective effect of spectra a and b. The signal consists of two doublets with one centered on zero frequency and the other being allowed to have some offset δ. The two doublets (Figure 3a,b) have different splittings (distance between peaks in a doublet), indicating that the attached and unattached segments are subject to different deformations. Therefore, the resulting NMR spectrum is asymmetric as shown in Figure 3c.

Our next step is to find out experimental evidence for the existence of the shifted spectrum of the segments closely associated with the carbon black as shown in Figure 3b. With increasing deformation of the polymer network the line splitting of the spectrum of Figure 3a,b will increase as indicated by the arrows. It is anticipated that the chains between the carbon black particles will experience a larger deformation, and so their splitting will increase more rapidly, revealing the off-resonance component. In principle, at a sufficiently large macroscopic deformation λ, a third or possibly fourth peak should become visible in the resultant spectrum (Figure 3c).

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 rf 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_0. The stretching ratio was determined from the distance between two marks on the sample, before and after stretching.

The partially deuterated poly(butadiene) was polymerized by a conventional Ziegler−Natta polymerization with toluene as solvent. The microstructure was determined by ^{13}C NMR and showed a 98% cis microstructure. Molecular weights

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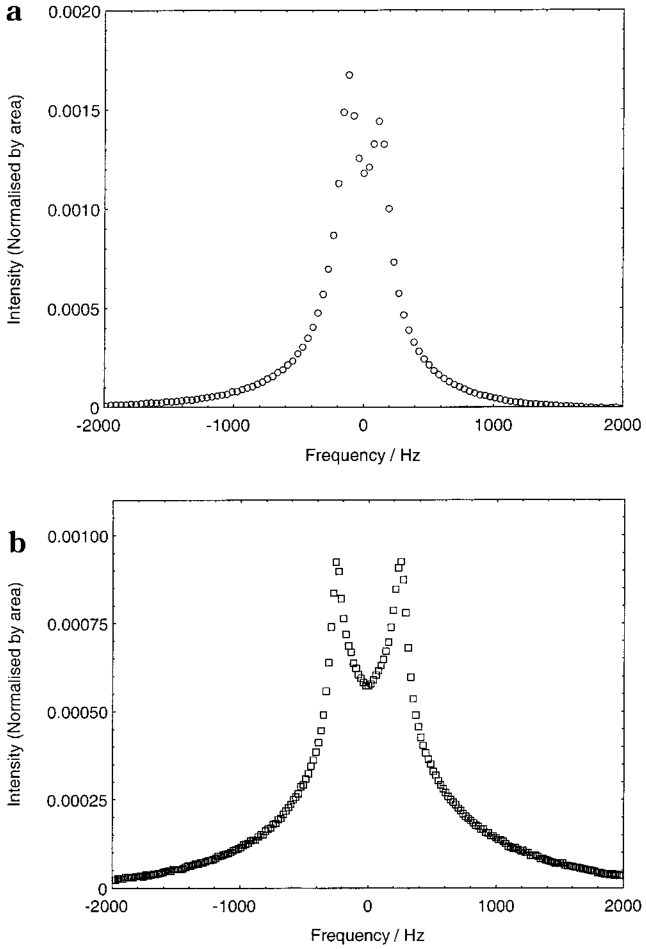

Figure 1. (a) NMR spectrum from a carbon black filled deformed poly(butadiene) network ($\lambda = 1.80$) showing the asymmetry in the peak heights. (b) NMR spectrum from an unfilled deformed network ($\lambda = 1.83$) showing the symmetry in the peak heights.

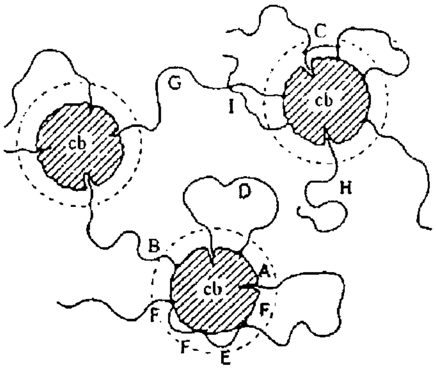

Figure 2. Model of the filler–elastomer interactions: cb, carbon black; A, physical attachment; B, chemical attachments; C, cross-linked rubber chain; D, loose fold; E, tight fold; F, multiple adsorptive attachments; G, interparticle tie chain; H, cilium; I, entanglements (from ref 4).

were determined by GPC (gel permeation chromatography): $M_n(D) = 25\,000$ g/mol, $M_w(D) = 120\,000$ g/mol, and a wide molar mass distribution ($U = 3.75$). This polymer was mixed in a ratio 1:9 with the nearly corresponding commercial nondeuterated poly(butadiene) BUNA cis 132 ($M_n(H) = 190\,000$ g/mol, $M_w(H) = 700\,000$ g/mol, $U = 3.68$).

Dicumyl peroxide (DCP) at 1 phr was used as the cross-linking agent for all networks prepared. Carbon black N220 was used as the filler. An amount of 25 phr of carbon black was incorporated by mixing the polymer, cross-linker, and filler together in a mixer of rotating frequency of 60 min^{-1} for 10 min at a temperature of 50 °C. The samples were vulcanized in a vulcameter press at 145 °C and 100 bar for 1 h. From mechanical stress–strain measurements[5] the resulting mean molar mass between two cross-links M_c is 6500 g/mol and the molecular weight between entanglements M_e is 1970 g/mol. Typically the sample size was 3.5 cm long, 0.5 cm wide, and 1.5 mm thick.

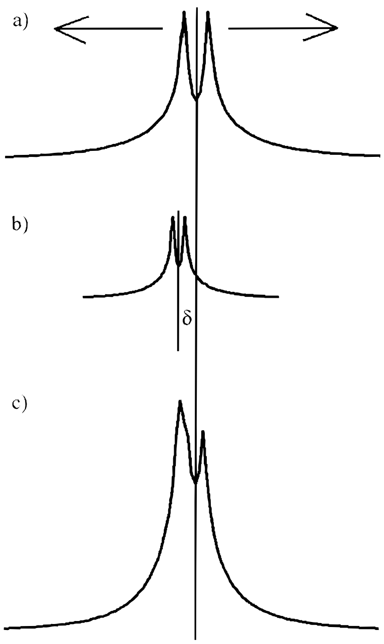

Figure 3. Schematic diagram showing how the resultant asymmetric NMR spectrum is formed from two symmetric signals. (a) NMR spectrum from segments not in the vicinity of the carbon black particles. (b) Signal from polymer chains that are close to carbon black filler particles and are therefore shifted by $-\delta$ Hz. (c) Collective effect gives rise to the resultant asymmetric NMR spectrum.

Background

Deuterium nuclear magnetic resonance (^{2}H NMR) has been used extensively to study the orientational order induced in rubber networks under uniaxial stress.[6–13] The spectrum of network chains exhibits a characteristic doublet structure. It is known that classical theories fail in giving a description for the existence of such a doublet structure.[14,15] This doublet structure has been attributed to orientational interactions between segments.[13]

However, the ^{2}H NMR line shape observed from carbon black filled elastomers is somewhat different from that of unfilled elastomers.[1] In the case of carbon black filled *cis*-1,4-poly(butadiene) networks it has been observed that the peaks of the spectrum of the Fourier transformed NMR signal are not equal in height; recall Figure 1a. No model in the literature for the NMR line shape from strained networks predicts this asymmetry. A similar situation was already stated by Gronski et al.[1] They observed that increasing the filler content of *cis*-1,4-poly(butadiene) network at constant deformation results in an overall broadening of the doublet line shape at nearly constant splitting and an increase in the asymmetry of the outer signal wings. To explain the above observations, they considered the filled network as consisting of two parts. One is formed by the pure rubber phase, whereas the second contains the filler and a fraction of rubber coupled in series. However, the proposed model, based on the free induction decay of the strained sample, which was approximated by superposition of two exponentials modulated by the frequencies of the quadrupolar splitting of the two rubber phases, was unable to explain the observed asymmetry.

In carbon black filled elastomers there exist three different spin−spin relaxation times (T_2), which have been associated with three microregions:[16,17] (1) a tightly adsorbed layer, where the motion of the chains is severely restricted surrounding the filler particles; (2) a more loosely bound domain; and (3) a third domain where the motion of the chains is similar to that of unfilled polymer. A recent investigation on the surface morphology of carbon black particles with an atomic force microscope suggests that rubber−filler interaction is likely to reflect strong topological constraints exerted by the carbon black complex surface on elastomer chains.[18]

Analysis

The two main ideas motivating this work are that (a) the chains in the vicinity of the filler particles have a different resonance frequency due to the susceptibility of the carbon black and (b) these chains experience a different deformation from that of the bulk sample due to their close attachment.

It is our intention to use an analytic result from the literature[2] for the line shape $G(\nu;\lambda,M_x)$ of a uniaxially deformed network. The analytic result is given in full in the Appendix. In this result ν is the NMR frequency in hertz, λ is the deformation, and M_x is the molecular weight between effective cross-links. This expression has been successfully employed in the analysis of unfilled poly(butadiene) networks.[2]

In our model we view the spectra as comprising two components: a signal from segments closely associated with the carbon black and those that are not. We will assume that the chains not in the local vicinity of the carbon black experience to a first approximation the macroscopic applied deformation λ. This means that the signal from these segments is fully specified by their effective cross-link density M_x and so simplifies the analysis by keeping the number of parameters to a minimum. Next we introduce a fraction f of signal that is from the segments closely associated with the carbon black (cb). As these chains are bound to the cb, we allow them to have a different effective cross-link density $M_{x,cb}$ and to experience a different local deformation λ_{cb}. The resultant signal $S(\nu,\lambda; f,\lambda_{cb},M_{x,cb},M_x,\delta)$ can be written as a linear combination of the two components

$$S(\nu,\lambda;f,\lambda_{cb},M_{x,cb},M_x,\delta) = (1 - f)G(\nu;\lambda,M_x) + f\,G(\nu-\delta;\lambda_{cb},M_{x,cb}) \quad (1)$$

where δ is the shift in the NMR frequency spectrum from the chains attached to the carbon black due to the local field strength difference (recall Figure 3b).

It is only under deformation that the NMR spectra become significantly asymmetric. The signals then clearly reveal that they have this off-resonance component. For successful analysis it is important to examine data that display enough features such that the parameters in the model can be reliably determined. If the deformation becomes too great ($\lambda > 2$) though, the theoretical result $G(\nu;\lambda,M_x)$, which is based on Gaussian statistics, is no longer valid.[2] For these reasons we begin our analysis with the $\lambda = 1.8$ data.

An Excel program has been written that minimizes the square of the difference between the theoretical signal and the experimental data. In Figure 4 we compare the resultant fit to the NMR spectrum from the network under deformation, $\lambda = 1.8$. The required fitting parameters are $M_x = 1600$ g/mol, $M_{x,cb} = 1100$ g/mol, $\delta = -49.8$ Hz, $f = 0.28$, and $\lambda_{cb} = 1.0$.

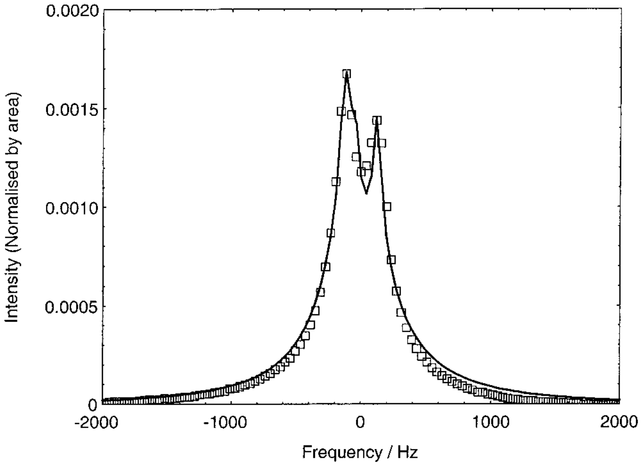

Figure 4. Solid line shows the theoretical fit of eq 1 to NMR spectrum from the strained poly(butadiene) ($\lambda = 1.80$) carbon black filled network. The required fitting parameters are $M_x = 1600$ g/mol, $M_{x,cb} = 1100$ g/mol, $\delta = -49.8$ Hz, $f = 0.28$, and $\lambda_{cb} = 1.0$.

This simple model is able to generate a reasonable fit to the experimental data (Figure 4). Better fits could have been obtained by adding more components corresponding to chains in a different environments; recall Figure 2.

The effective cross-link density of the chains not in the vicinity of the carbon black particles was found to be 1600 g/mol. This can be compared with the stress−strain measurements.[5] In this work it was found that the molecular weight between chemical cross-links M_c was 6500 g/mol and entanglements M_e was 1970 g/mol. The molecular weight between effective cross-links M_x can be estimated from the relationship[19]

$$\frac{1}{M_x} = \frac{1}{M_e} + \frac{1}{M_c} \quad (2)$$

From this a value for M_x of 1500 g/mol is determined. This is very close to the above found fitting parameter and indicates that the theoretical function $G(\nu;\lambda,M_x)$ is correctly describing the NMR response.

The cross-link density of the chains closely attached to the carbon black particles was found to be 1100 g/mol. This again is in good agreement with the estimated value for the cross-link density found from eq 2. This slightly higher density of cross-links is consistent with the chains being attached to the filler particles and these contacts acting as extra cross-link points. It is also interesting to note that the effective deformation for these chains was $\lambda_{cb} = 1.0$. This reveals that these chains remain essentially isotropic and do not directly take part in the bulk deformation, due to their close attachments to the filler particles.

In addition, the fit based on eq 1 gives direct access, through the parameter $f = 28\%$, to the amount of polymer chains in the vicinity of the filler particles. This value compares favorably with work by Gronski et al.[17] on carbon black filled networks. They fitted the proton NMR relaxation after a solid echo using three Gaussian

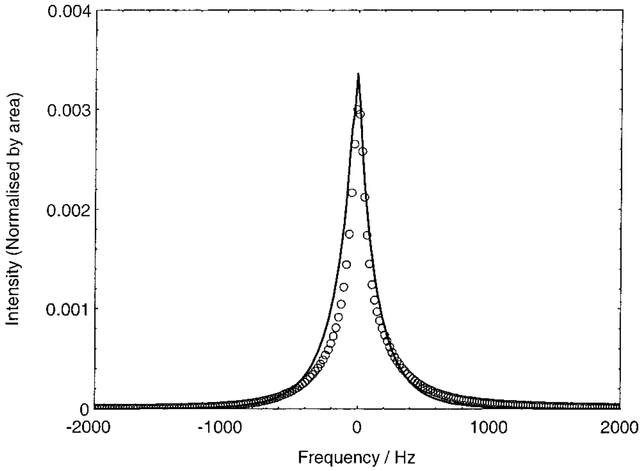

Figure 5. Solid line shows a no free parameter fit of eq 1 to the NMR spectrum from the undeformed poly(butadiene) carbon black filled network.

Table 1. Carbon Black Electron Spin Concentrations and Mass Susceptibilities

carbon black	mol %	spin concn $\times 10^6$	mass susceptibility $\times 10^6$ net	paramagnetic	diamagnetic
N550	95.77	10.0	−0.82	0.21	−1.03
N330	95.75	8.0	−0.79	0.17	−0.96
N220		9.2	−0.76	0.19	−0.95
N110	94.78	8.1	−0.73	0.17	−0.90

components. They attributed these components to segment in different regions within the sample (Figure 2), giving a measure of the fraction of chain closely associated with the carbon black particles.

Kraus and Collins measured the magnetic susceptibilities and spin concentrations for a range of different carbon blacks.[3] Their data are shown in Table 1. They also broke down the mass susceptibility values into their respective diamagnetic and paramagnetic components—this being derived from the spin concentration and susceptibility of free electrons. We then use the net magnetic susceptibility χ to estimate a value for the frequency shift Δf produced by carbon black N220 of −47 Hz via

$$\Delta f = \chi \times 61.3 \text{ MHz}$$

This is only an estimation of the frequency shift as it does not take into account the influence of the geometry of the filler particle on its local field. The frequency shift $\delta = -50$ Hz determined by fitting of the eq 1 to the experimental data though is in good agreement with this estimated value.

Now that the microscopic parameters (M_x, $M_{x,cb}$, f, λ_{cb}) have been determined from the analysis of a NMR spectrum from the deformed network ($\lambda = 1.8$), they can now be used to generate the theoretical signal from the undeformed sample. Figure 5 compares the data from the unstrained network $\lambda = 1.00$ and the theoretical signal using the above found parameters. For a no parameter fit the theory compares favorably to the data. It would have been possible to achieve better fits by simultaneously fitting the NMR data from $\lambda = 1.00$ and the $\lambda = 1.80$ deformed networks, but our approach is a stronger test of this off-resonant component model.

It is possible to make a prediction using our model and the microscopic parameters found from the analysis of the $\lambda = 1.80$ data. At sufficiently high enough deformations the splitting from the chains that are not closely attached to the carbon black particles should become large enough so as to reveal unambiguously the off-resonance component. In Figure 6a we show the theoretical spectrum from a sample at deformation $\lambda = 2.5$, using the parameters found from the above analysis. Here a third peak can be seen in the theoretical response corresponding to the isotropic off-resonance component. In Figure 6b we show the NMR spectrum measured from a network at a high deformation, $\lambda = 3.00$. Here it can be seen that the experimental data do reveal this off-resonance component, which qualitatively our theoretical function does. We do not attempt to quantitatively analyze these data as the theoretical function used is only strictly correct for deformations $\lambda < 2$, which is within the validity of the Gaussian chain approximation.

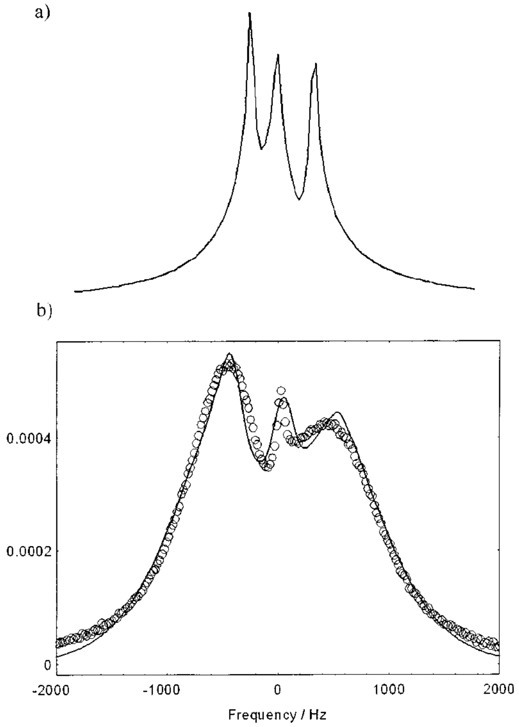

Figure 6. (a) Theoretical spectrum from eq 1, with the parameters found from fitting the $\lambda = 1.80$ network data, predicts the emergence of a third peak to be found at high deformation ($\lambda = 2.5$). (b) This third peak is found experimentally at deformations of $\lambda = 3.00$ in the NMR spectra of the carbon black filled poly(butadiene) network. The solid line represents a phenomenological fit to the data points.

The solid line in Figure 6b is a fit to the data using a phenomenological function consisting of a broad and narrow doublet. Each doublet is constructed from two stretched exponentials with the form $\exp(-|\nu/w|^n)$, where w and n are fitting parameters. One of the doublets is allowed to be off-resonance, i.e., not centered at 0 Hz (recall Figure 3), simulating the effect of the carbon black susceptibility. Figure 6b illustrates that at even the highest deformation the observed asymmetry can be reconstructed using the idea of an off-resonant narrower component as proposed by this paper. It must be noted though that the frequency offset determined from this phenomenological analysis was 175 Hz, as opposed to the previously found 50 Hz from the least-squares analysis of the $\lambda = 1.80$ data. Indeed, all the data can be fitted using this larger frequency offset.

Conclusions

In this paper we showed that the asymmetric NMR spectra observed from strained filled networks could be explained by considering the susceptibility of the carbon black particles. Polymer segments closely associated with the filler particles experience a different local field and contribute an off-resonance term to the free induction decay. In the NMR spectrum this appears as a frequency shifted component relative to the non-closely attached chain signal. The resultant spectrum is then asymmetric.

We applied the theoretical work of Brereton and Ries[2] to model the NMR line shapes quantitatively. A very simple approach was adopted in that the signal was considered to comprise of only two components: polymer segments closely attached to the carbon black particles and those that are not. It was found that the signal from the attached chains needed to be off-resonance by −50 Hz, with this comparing extremely well with susceptibility measurements on carbon black.[3] The cross-link density determined from this analysis was in close agreement with the stress−strain measurements on this sample.[5] The fraction of signal attached to the carbon black was found to be 28%, with this being in reasonable agreement with other NMR work on similar filled networks.[17] An interesting point is that the chains attached to the carbon black experience a different local deformation to that from the bulk sample, with these segments remaining isotropic.

As a test of this two component model, we used the parameters determined from the analysis of the $\lambda = 1.8$ data to predict the undeformed network result. It was found that for a no free parameter fit that the theory and data were in good agreement (see Figure 5). It is interesting to note that the undeformed sample shows little asymmetry and that this off-resonance component also theoretically remains somewhat hidden at low deformations.

From our model a prediction was made that at high deformations the isotropic off-resonance component will become visible as a third peak in the NMR spectrum. This was illustrated qualitatively by the theoretical function (eq 1) in Figure 6a. In Figure 6b data from a highly deformed filled network ($\lambda = 3.0$) are shown for comparison, where this predicted third peak can clearly be seen.

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Appendix

Ries et al. have recently published an analytic expression for the NMR frequency response from a uniaxially strained polymer network.[2] The theoretical line shape $G(\nu;\lambda,N)$ is dependent on the number of statistical segments between effective cross-link points, N, the rescaled quadrupolar interaction strength, ν_0, the deformation λ, and the ratio, b/ξ, of the statistical segment size to the Edwards screening length, through

$$G\left(\nu;\lambda,N,\nu_0,\frac{b}{\xi}\right) = \left(\frac{3N\pi}{2\nu_0}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\left[g_+\left(\left|\nu\right| + \frac{\Delta\nu}{2}, \lambda\right) + g_-\left(\left|\nu\right| - \frac{\Delta\nu}{2}, \lambda\right)\right] \tag{A1}$$

where

$$\Delta\nu = \frac{2}{15\pi}\frac{\nu_0}{N}\frac{b}{\xi}\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{A2}$$

with

$$g_+(\nu,\lambda) = \exp\left[-\frac{3N\pi\lambda}{\nu_0}\nu\right] \tag{A3}$$

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

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_0}\nu\right] \tag{A4}$$

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

$$g_-(\nu,\lambda) = \exp\left[\frac{3N\pi\lambda}{\nu_0}\nu\right]\left\{1 - \mathrm{erf}\left[z(\nu)\sqrt{\frac{3}{2}\left(2\lambda + \frac{1}{\lambda^2}\right)}\right]\right\} \tag{A5}$$

with

$$z(\nu) = \sqrt{\frac{N\pi\nu}{\nu_0}} \tag{A6}$$

In this work we are considering a methylene-labeled poly(butadiene) network. Our previous studies on these systems have determined several of the above-mentioned parameters.[2,20] The size of the NMR statistical segment was found to be 260 g/mol, which means that N can be more usefully expressed in terms of the effective molecular weight between cross-link points M_x as $N = M_x/260$ (g/mol). A value of 7730 Hz was determined for ν_0. From the dependence of the splitting on deformation the ratio of $b/\xi = 6.0$ was found. The function used in the paper is defined through eq A1 by $G(\nu;\lambda,M_x) \equiv G(\nu;\lambda,(M_x/260 \text{ g/mol}),7730,6.0)$.

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