Influence of Polymer Chain Concentration and Molecular Weight on Deformation-Induced ^{2}H NMR Line Splitting

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ABSTRACT: Deuterium nuclear magnetic resonance line splitting arising from deformed *cis*-1,4-poly(butadiene) network, of which the network chain concentration is varied by incorporating protonated free chains of similar kind, is investigated. The results are discussed according to the theoretical framework, introduced by Brereton and Ries,[1] which dealt with network vectors which were treated as quenched variables, to show explicitly how they collectively determine the anisotropy in the mean field. The influence of the network chain concentration on the NMR line splitting and molecular weight dependence of Flory interaction parameter χ and the possibility of using the deuterium NMR line splitting to investigate χ parameter of a system are discussed.

Introduction

When a deuterated network is stretched, an oscillation, corresponding to a splitting in frequency space, is produced in the transverse deuterium NMR decay[2] (see Figure 1).

This indicates an anisotropic orientation of the chain segments translated through the junction points. However, Brereton[3] and Sotta and Deloche[4] showed that for a noninteracting (phantom) network the oscillations from individual chain segments, when averaged over all network chain orientations, give rise to a nonoscillating signal and consequently a single (broadened) line shape. The doublet line shape seen in the frequency domain was therefore indicative of a higher degree of anisotropy than that induced merely by the cross-link points. This is further confirmed by the interesting observation that deuterated free chains within a protonated deformed polymer network exhibit approximately the same line splitting as a deuterated deformed network. The situation is schematically represented in Figure 2.

An oscillation in the free chain signal reveals that the splitting does not depend explicitly on the presence of cross-links; i.e., the constraint arising from the network due to cross-links is not responsible for the line splitting. Similar observations have been reported in the literature from deuterated solvent molecules within a protonated deformed poly(dimethylsiloxane) (PDMS) network.[5−7] Sotta et al. demonstrated that when oligomers of deuterated PDMS were dissolved into a uniaxially deformed PDMS network, they also showed the characteristic doublet.[8] Further, these oligomers displayed the usual orientational dependence ($3\cos^2\theta - 1$) of their splitting on the angle θ between the applied strain and the magnetic field. This clearly revealed that all the chains in the sample, both network and free chains, were aligned along the strain direction.

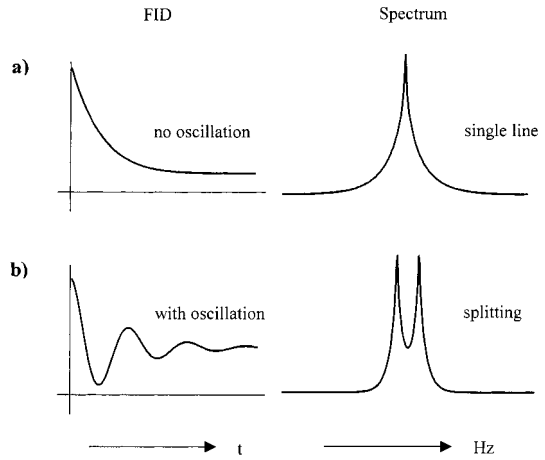

Figure 1. NMR response in time domain and after Fourier transformation: (a) free induction decay (FID) without oscillation corresponds to a single line while (b) FID with oscillation corresponds to a splitting indicating that the deuterium NMR line splitting is solely due to the oscillations in FID.

Previously, Sotta and Deloche[8] introduced nematic interactions occurring between neighboring segments to explain this phenomenon. These nematic interactions would both enhance the anisotropy of the network segments and generate it in any dissolved free chains. In a later work Brereton[3] showed that it was sufficient to include only excluded-volume interactions in order to account for the observed line splitting. For the network these were treated as the mean field level, and it was shown that an anisotropic mean field arises when the network is deformed. Subsequently, numerical simulations[9,10] on deformed one-component systems have demonstrated the ability of excluded-volume interactions to produce the experimentally observed splitting.

A general analytic result that includes the effect of anisotropic mean field and network constraint was derived in our previous work.[11] It was shown, from analyzing a range of deformed network sample signals,

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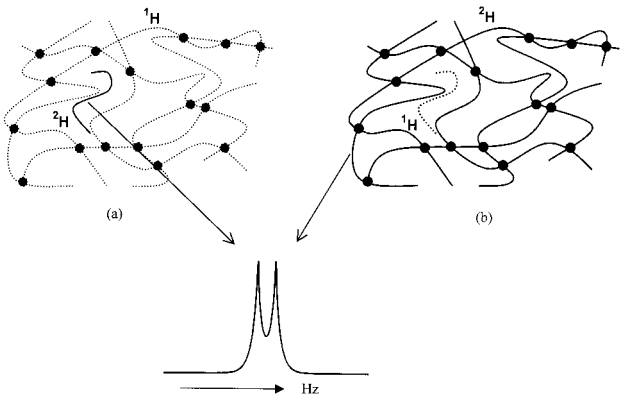

Figure 2. Schematic representation of (a) deuterated free chains in a protonated polymer network and (b) protonated free chains in a deuterated polymer network. The black circles are to represent chemical and physical cross-links in the network. It is shown that a small amount of deuterated free chains in a deformed protonated network shows almost the same line splitting as that from pure dry deuterated network at the same deformation ratio.

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. In a network a polymer segment interacts with many neighboring ones. These many interactions can be described by an effective mean field.[12,13] NMR is able to monitor the average orientation due to the cross-links and this mean field separately, allowing the two contributions to the total average orientation $\overline{P_2(\cos\theta)}$ to be evaluated.[11]

The mean field was expressed in terms of excluded-volume interactions. A theoretical interpretation by Brereton and Ries[1] 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 V, an anisotropic mean field. All chains, network or free, within the rubber matrix experience this mean field that causes an additional induced alignment along the strain direction. The resultant splitting due to this interaction is dependent on the size of the excluded-volume interaction V.

In this paper, the Brereton−Ries approach is discussed and shown how it can be used to interpret the experimental observations. It will also be shown that the splitting on either kind of chain (network or free) for a uniaxial extension λ varies linearly with $\lambda^2 - 1/\lambda$. The magnitude is determined by the mean field, which can be experimentally controlled by blending the network with free chains. For free chains, identical to the network chains, the principal effect is simply to dilute the contribution to the mean field from the network chains. A more interesting contribution to the mean field arises from free chains of a different chemical nature. This is compared with the experimental results.

Network Probe and Free Chain Probe

The splitting is dependent on the network fraction and determined by the excluded-volume interaction as expressed by the ratio of the Edward's screening ξ to the chain segment length b. It has shown[1] that the deuterium NMR line splitting $\Delta\nu_{A/B}$ from either the network (A) or free chains (B) can be written as

$$2\pi\Delta\nu_{A/B} = 2(\lambda^2 - \lambda^{-1})\Delta_{A/B} \tag{1}$$

The deformation dependence is entirely contained in the prefactor, whereas the molecular weight, concentration, and temperature dependence are contained in the term $\Delta_{A/B}$, given by

$$\Delta_{A/B} = \frac{2}{15\pi}\frac{1}{cb^3}\frac{v_0}{N_A}\frac{c_A}{c}\left[\frac{b}{\xi} + \frac{c_B}{c}F_{A/B}\right] \tag{2}$$

where

$$F_A = \frac{\sqrt{12}\left(\frac{1}{N_B} - \frac{1}{N_A} - 2c_B\chi\right)\left(\frac{1}{N_B} + 6\left(\frac{c_A c_B}{c}(\chi_0 - \chi) - 2c_B\chi\right)\right)}{\left[\frac{2c_A c_B}{c}(\chi_0 - \chi)\right]^{3/2}} \tag{3}$$

$$F_B = \frac{\sqrt{12}\left(\frac{1}{N_B} - \frac{1}{N_A} + 2c_A\chi\right)\left(\frac{1}{N_B} + 6\left(\frac{c_A c_B}{c}(\chi_0 - \chi)\right)\right)}{\left[\frac{2c_A c_B}{c}(\chi_0 - \chi)\right]^{3/2}} \tag{4}$$

Here N_A and N_B are numbers of statistical segments per chain (network and free, respectively); c_A, c_B, and c are concentrations of network chain, free chain, and total, respectively

$$2\chi_0 = \frac{1}{c_A N_A} + \frac{1}{c_B N_B}$$

There are two contributions to the splitting given by eq 2. Contribution of the first term, i.e., b/ξ, is of the order of 1, and the contribution of the second term, i.e., $F_{A/B}$, is of the order of $1/N_A$. If the network chains and free chains are chemically identical but of different molecular weights (i.e., $N_A \neq N_B$, $\chi = 0$), the second term becomes (from eqs 3 and 4)

$$F_{A/B} = \frac{\sqrt{12}\left(\frac{1}{N_B} - \frac{1}{N_A}\right)\left(\frac{1}{N_B} + 6\left(\frac{c_A c_B}{c}(\chi_0)\right)\right)}{\left[\frac{2c_A c_B}{c}(\chi_0)\right]^{3/2}} \tag{5}$$

and is the same for both kinds of chains. That means the line splitting is the same from network and free chains.

Experimental Section

The synthesizing and vulcanization procedure, and the molecular parameters of *cis*-1,4-(polybutadiene) network, which is used in this study, have been described elsewhere.[11,14] The resulting mean molar mass between two cross-links, $M_c = 6500$ g/mol, was determined from mechanical stress−strain measurements[15] and NMR relaxation.

A Varian INOVA 400 wide bore spectrometer (400 MHz proton frequency), operating at 61.3 MHz for deuterons and at room temperature, was used to perform all NMR experiments. The deuterium NMR spectra were obtained by applying a standard 90° radio-frequency pulse of approximately 6 μs in width. The mechanical deformation to the sample was performed by a simple stretching device which stretch the

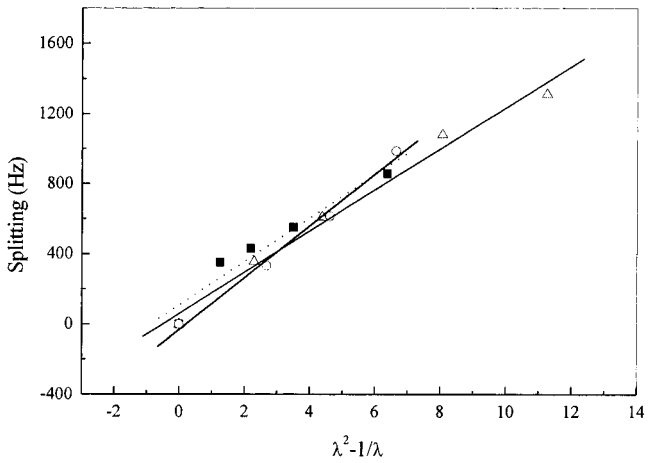

Figure 3. Comparison of the line splitting from a deuterated dry network and from deuterated free chains (M_n = 25 000 g/mol) within protonated networks: (■) deuterated dry network (M_C = 6500 g/mol); (△) deuterated free chains dissolved in protonated network (M_C = 8000 g/mol); (○) deuterated free chains dissolved in protonated network (M_C = 10 000 g/mol). The straight lines correspond to linear curve fits of the individual data sets. The slight deviation of the splitting observed from free chains to that of dry network is due to the different M_C values of the networks.

specimen in parallel to the static magnetic field B_0. The stretching ratio was determined by measuring distance, before and after stretching, between two marks on the sample.

Results and Discussion

^{2}H NMR line splitting of three different networks is shown in Figure 3. Two of the polymer networks are fully protonated (average mean molecular mass between two cross-links M_C = 10 000 and 8000 g/mol), and they were incorporated with deuterated free PB chains of M_n = 25 000 g/mol. The free chain incorporation procedure was a simple one: free chains were laid firmly on the network and allowed enough time (few weeks) to be well incorporated to the network. Finally, the remaining free chains on the surface were wiped out.

For comparison, the line splitting of a deuterated dry network (M_C = 6500 g/mol) is also shown in Figure 3. The magnitudes of the splitting for all components, the signal from the free chain or network, are comparable and have the same dependence on extension ratio ($\lambda^2 - 1/\lambda$). The straight lines are individual best linear fits to the experimental data sets. The difference in M_C values of each network causes the slight deviations of the slopes.

The next step was to study how the ^{2}H NMR line splitting is affected by network concentration c_A. The network volume fraction of a deuterated PB dry network (M_c = 6500 g/mol) was gradually reduced by inserting protonated free chains of M_n = 1800 g/mol to the network. Deuterium NMR line splitting was measured at different network concentrations. The effective molecular mass M_x ($1/M_x = 1/M_c + 1/M_e$, where M_e is the average molecular mass between two entanglements) of the above dry PB network, determined by deuterium NMR line shape analysis, is 900 g/mol.[11] Since the mass of a statistical segment of methylene deuterated PB is 260 g/mol,[15] it is calculated the N_A to be 3.5. The number of statistical segments of the protonated free chains N_B is calculated to be 6.9. In an earlier work[11,15] it has shown that the ratio of the length of a statistical segment to Edward's screening length, b/ξ, is 6.0 and

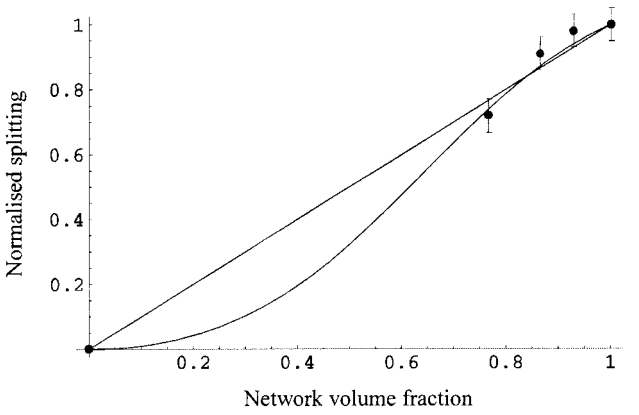

Figure 4. Magnitude of the splitting, normalized to the dry network, for deuterated strained *cis*-1,4-poly(butadiene) network which is incorporated with protonated free chains of different length as to the network, as a function of network volume fraction. The continuous lines are according to the analytical result. The straight line is the linear dependence of line splitting without including the χ-dependent part.

ν_0 = 7730 Hz. Using these values and eqs 1−3, the experimental data of the network concentration dependence of line splitting were fitted to the theoretical function (eq 1) for λ = 1.8 and are shown in Figure 4. A slight deviation from the usual linear dependence of the splitting on network concentration is observed. The difficulty of obtaining more experimental data points lies in the long time it takes to dissolve polymer chains of sufficient length to be considered as a statistical chain into a network. In the case of χ = 0 (i.e., there is no role of Flory interaction parameter), the theoretical curve shows the linear dependence. However, when $\chi \neq 0$, the second term of eq 2 is beginning to compete with the Edward's screening length. This is because a small Flory interaction parameter has been introduced due to the slight dissimilarity between the deuterated chemically cross-linked chains and the protonated chains.

According to the experimental results, depicted in Figure 4, F_A is initially negative and then crosses over the linear dependence to the positive values. At the point of this interception with linear dependence the numeric value of F_A becomes zero. This situation can only be realistic, according to eq 3, when

$$\frac{1}{N_A} - \frac{1}{N_B} - 2c_B\chi = 0$$

c_B (when F_A = 0) is estimated using experimental results as 0.2. Therefore, while knowing N_A and N_B, χ is calculated to be 0.35. Using these values, data can be modeled as a no parameter fit to eq 1 and where the splitting from the network has been normalized to a dry network result.

In a similar work Sotta et al.[5] used a system of deuterated PDMS polymer chains, of the same molecular weight to that of the cross-link density, which are dissolved into a protonated polymer network. The experiments were done at a series of concentrations of the free chains. We use the data published in that work to model the analytical expression. Since free chains are the NMR probe molecules (i.e., deuterated), eq 4 has to be used to model the contribution to the splitting arising from χ. All the parameters for this PDMS system are known:[5] $N_A = N_B = 16$, $\xi = b/4$, ν_0 = 21 kHz, and hence this enables the measurement of the Flory interaction term χ. The data can be modeled by a constant χ = 0.09

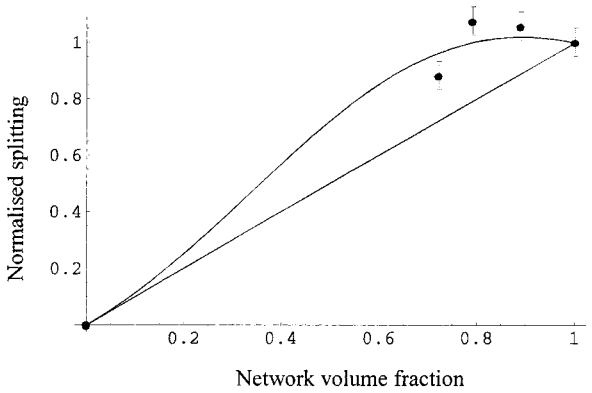

Figure 5. Magnitude of the splitting, normalized to the dry network, for protonated strained PDMS network which is incorporated with deuterated free chains of the same length as the network chains, as a function of network volume fraction. The contineous lines are according to the anlytical result. The straight line is the linear dependence of line splitting without including the χ-dependent part.

(see Figure 5), where the splitting from the free chains has been normalized to that of dry network.

Although the chemically structural difference (protonated and deuterated) in the cases of PDMS and PB are almost the same, there exists a large difference in the effective molecular weights between cross-links M_x. It was 6500 g/mol for the PDMS[5] and 900 g/mol for the PB. So that the difference of M_x is about 7 times. The difference of the cross-link densities of PDMS and PB may result in the different values of the χ parameter.

During a study on swelling in cross-linked natural rubber, McKenna et al.[16] have shown experimentally that the magnitude of χ depends on cross-link density, and furthermore, the value of χ in the cross-linked polymer was a linear function of the cross-link density. In the same study it has shown the variation of χ with volume fraction of rubber.

Therefore, it is argued here that the apparent increase of χ in the system of poly(butadiene) is due to its higher cross-link density than that of PDMS. Additionally, this opens a new way to investigate χ using deuterium NMR spectroscopy.

Summary

Deuterium nuclear magnetic resonance line splitting arising from the deformed *cis*-1,4-poly(butadiene) network, of which the network chain concentration is varied by incorporating protonated free chains of similar kind, is investigated. The results are discussed according to the analytical result by Brereton and Ries,[31] which dealt with network vectors which were treated as quenched variables, to show explicitly how they collectively determine the anisotropy in the mean field.

It is shown that the network chain concentration directly influences to the magnitude of observed deuterium NMR line splitting while the chemical nature and the length of the network and free chains playing a minor role. However, by analyzing the results, it is shown that the Flory interaction parameter χ has a direct influence from the chain length. As a result, this study paves a way also to investigate χ parameter of a system using deuterium NMR line splitting.

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