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Short Communication

Deformation behavior of elastomeric networks studied by deuterium nuclear magnetic resonance (^{2}H NMR)

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Abstract

Deuterium nuclear magnetic resonance (^{2}H NMR) was used to test a theoretical framework that has been introduced to explain the ^{2}H NMR line splitting of uniaxially stretched partially deuterated poly(butadiene) elastomers. The theory attributes the higher degree of anisotropy implied the splitting to the interchain steric interactions. 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.

1. INTRODUCTION

Rubbers are important materials for numerous applications. Nuclear magnetic resonance (nmr) allows one to relate macroscopic properties to microscopic behavior of polymeric chains via the presence of residual interaction, due to local order related to the constraints resulting from crosslink junctions. ^{2}H-nmr has been devoted to be a sensitive and powerful tool to study this anisotropy at a molecular level in strained elastomers. For unreformed rubbers a single resonance line is observed. Under uniaxial deformation the spectra splits into a well-defined doublet structure. A non-interacting Gaussian phantom network has been theoretically shown to generate no splitting under deformation [1]. These results therefore indicate that to model the chain reorientation in

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a strained elastomer one must introduce chain interactions. A theory by Brereton and Ries [1] attributes the higher degree of anisotropy implied the splitting to the interchain steric interactions. Under deformation the distribution of monomeric segments generates, through their isotropic steric interactions, an anisotropic mean field which causes an induced alignment with the strain direction. The resultant splitting due to this interaction is dependent on the size of the excluded volume through the Edwards screening length.

2. EXPERIMENTAL

All experiments were carried out on a Varian Unity 400 spectrometer at 61.3 MHz for deuterons at room temperature. Spectra were obtained using standard 90^0 rf pulse (7 μs). 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 elastomers were based on partially CD_2 – deuterated poly (butadiene) PB-d_4 with cis/trans/vinyl-microstructure, different precursor molar mass and a narrow mass distribution. An amount of 0.5 phr Dicumyl peroxide (DPC) was used as crosslinker for all networks under study. The samples were vulcanized in a vulcameter press at 145 ºC and 100 bar for 1h.

3. THEORY

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 R formed by two consecutive crosslinks determines a static residual average orientation of the labeled bond. Secondly there are the interactions ν of the chain segments in the rubber with their many neighbors. A theoretical framework is developed [2] in order to show that the free induction decay separates the contribution to the orientation arising from the network constraint to that from chain interactions:

$$G(t,\lambda) = \mathrm{Re}\left\{\exp\left[2i\nu_o \left\langle P_2(\cos\theta)\right\rangle_V t\right] \times \overline{\exp\left[2i\nu_o \left\langle P_2(\cos\theta)\right\rangle_{\mathbf{R}}\right]} t\right\} \tag{1}$$

The first term of equation (1) corresponds to an oscillation, or a splitting, whose frequency depends on the mean field contribution to the average. It is shown that the NMR spectrum can be determined from

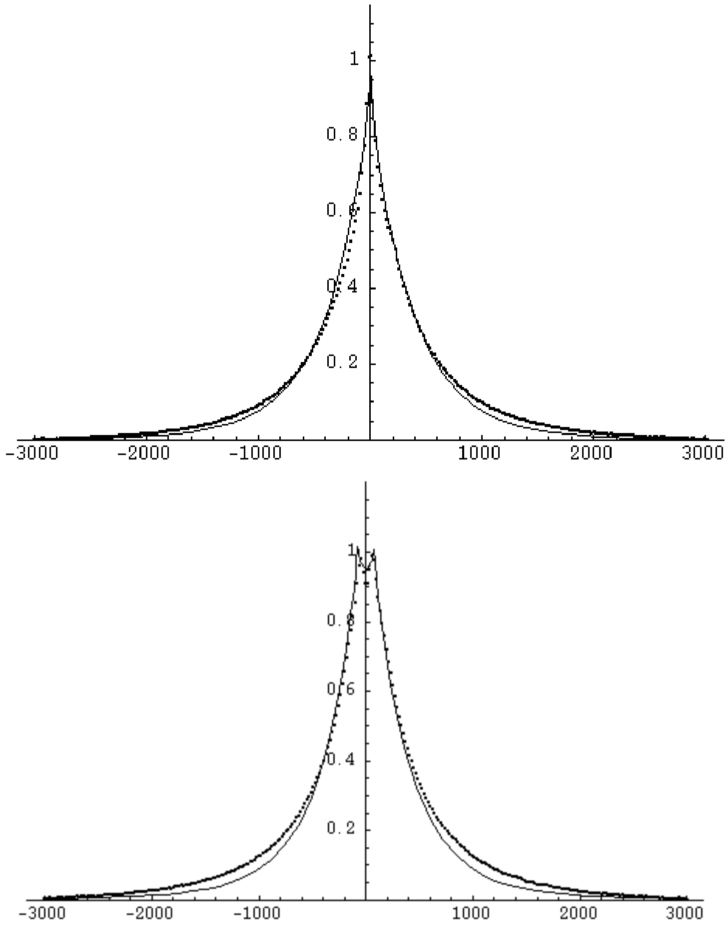
$$G(\nu,\lambda) = \left(\frac{3N\pi}{2\nu_o}\right)\left[2\lambda + \frac{1}{\lambda^2}\right]^{-1/2}\left[g_+\left(|\nu| + \frac{\Delta\nu}{2},\lambda\right) + g_-\left(|\nu| - \frac{\Delta\nu}{2},\lambda\right)\right] \tag{2}$$

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

For a more detailed explanation see reference [2] and [3].

4. RESULTS AND DISCUSSION

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 ^{2}H line shape and the splitting has been fitted simultaneously for a range of deformed poly (butadiene) networks in dependence on λ. All ^{2}H nmr spectra could be described with only three independent parameters: the rescaled quadrupolar interaction divided by the number of statistical segments v_0/N, the magnitude of splitting in the frequency space Δv that depends on the mean field contribution to the anisotropy through equation (2a) and the deformation ratio λ.



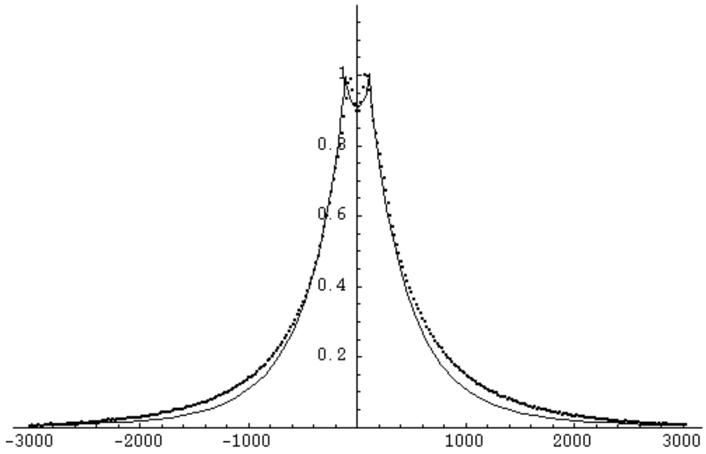


Figure 1: Experimental ^{2}H nmr spectra and the fit by equation (2) for a network with 0.5 phr DCP at λ=1.0(top), λ=1.1(middle) λ=1.2 (bottom).

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 crosslinks M_{eff} ($M_{eff} = 1/M_C + 1/M_{Entanglement}$) which contains the topological hindrance due to crosslinks and entanglements and the size of the segmental interactions, which we choose to express in terms of the Edwards' screening length. Brereton and Ries [1] had shown that the average orientation due to this anisotropic screened potential $<P_2(\cos\Theta)>_v$ is depending only on the crosslink density and the ratio b/ἑ. 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. The ratio v_0/N was estimated to be 5200, 5100, 3800 and 3700 Hz for the 4 different networks. This trend is in good agreement with the G'-modulus measurements. The value of the corresponding rescaled interaction constant v_0 for methylene deuterium (7730 Hz) and the molecular weight of a nmr statistical segment ((260+-30/294*) g/mol) was taken from poly (butadiene) melts [4]. Then 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_E was found to be about 1700 g/mol for the given microstructure. The expected effective molar masses M_{eff} were calculated as 1120, 1160,1360 and 1290 g/mol for the networks which is close to the above nmr determined value for the effective molecular weight. The ability of the theoretical result to measure a crosslink density that compares well with mechanical tests [4] and a screening length of a reasonable 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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