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Mean Field Contribution to the Average Segmental Orientation of a Polymer Network Studied by Deuterium Nuclear Magnetic Resonance: Temperature Dependence

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Deuterium nuclear magnetic resonance (^{2}H NMR) has been used extensively to study the orientational order induced in rubber networks under uniaxial stress.[1−3]

For an undeformed rubber a single resonance line in the deuterium NMR spectrum is observed.[4] Under uniaxial deformation the spectrum splits into a well-defined doublet structure corresponding to an oscillation in the free induction decay.[5] A noninteracting phantom Gaussian network theoretically shows no splitting under deformation.[6] These results therefore indicate that to model the chain reorientation in a strained elastomer one must include segmental interactions.[7] In strained rubbers there is a higher degree of anisotropy than that merely induced by the cross-links.

Several explanations have been put forward to account for the oscillations seen in the free induction decay from strained deuterated networks; these include nematic interactions,[8] excluded-volume interactions,[9] and anisotropic junction fluctuations.[10]

In a previous[11] work, it has shown that the oscillations are indicative of an anisotropic mean field due to the many segmental interactions. Furthermore, the decay envelope of the oscillations reveals the distribution of network vectors—each formed by connecting together consecutive cross-links. A general analytic result that includes the effect of anisotropic mean field and network constraint was derived. It was shown, from analyzing a range of deformed network sample signals, 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[9] 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 within the rubber matrix experience this mean field that causes an induced alignment along the strain direction. The resultant splitting due to this interaction is dependent on the size of the excluded-volume interaction. We have calculated[11] the average orientation due to this anisotropic mean field, $\langle P_2(\cos\theta)\rangle_V$, as

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

where ξ is the Edwards' screening length and N is the number of Gaussian statistical segments of average size b between the junction points.

The screening length ξ can be expressed in terms of V and b as

$$\xi = b\sqrt{\frac{kT}{12Vc}} \tag{2}$$

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

The b/ξ is expected to be a constant for a given polymer and should be independent of the network cross-link density. In one of our subsequent works[14] it was shown that b/ξ was independent of the cross-link density, giving further support to the above theoretical framework.

Our next aim is to find evidence for the temperature dependence of anisotropic mean field $\langle P_2(\cos\theta)\rangle_V$. Only a few studies have been reported in the literature concerning the temperature dependence of the deuterium NMR line splitting. The main fact that hinders such investigation is the very low sensitivity of line splitting to the temperature, and so a large temperatures range needs to be examined. This is restricted by the appearance of crystallites at low temperatures and the difficulty of gripping the sample at high temperatures.

In an earlier work by Deloche and Samulski[15] considering nematic-like interactions between chain segments, it was reported that the segmental order parameter S, which is measure of the average orientation, will have a dependence on temperature according to

$$S = S^*{}_{\mathrm{seg}}\left(1 + \frac{\phi E}{\alpha(T - T^*)}\right) \tag{3}$$

where S^*_{seg} is the ideal segment order parameter deduced from kinetic theories of rubber elasticity,[16] ϕ is the rubber volume fraction, E is a constant related to elastic modulus, and α is a constant related to the interactions between segments.

T^* in eq 3 corresponds to a critical temperature of the polymer sample. In the present study T^* can be considered as the glass transition temperature. Since the experiments are conducted at a temperature (−20 to +60 °C), which is well above the glass transition

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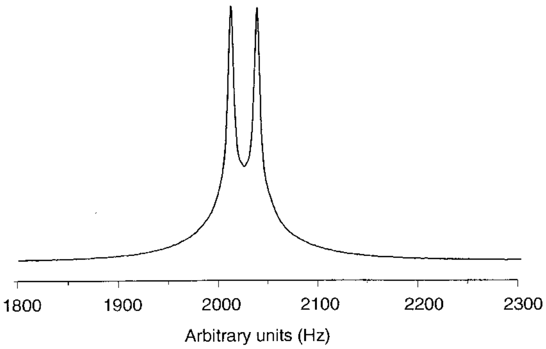

Figure 1. Deuterium NMR spectrum observed from partially deuterated *cis*-1,4-poly(butadiene) network (deformation ratio $\lambda = 1.48$ and temperature $T = 27$ °C). The line splitting $\Delta\nu$ is determined by taking the separation between maximum points of the spectrum.

temperature (~−105 °C), this term can therefore be neglected. Hence, the segmental order parameter has the predicted temperature dependence $1/T$. The NMR line splitting $\Delta\nu$ is related to S according to the relation[17]

$$S = 8\Delta\nu/\nu_q \tag{4}$$

where ν_q is the static quadrupolar interaction constant. From the above formulations by Deloche and Samulski it can be revealed that $\Delta\nu$ has an expected temperature dependence of $1/T$.

According to Brereton and Ries,[9] the term b/ξ (in eq 1) is the temperature-dependent part of the deuterium NMR line splitting. The line splitting depends on temperature as $1/\sqrt{T}$ as can be seen from eqs 1 and 2, i.e.

$$\langle P_2(\cos\theta)\rangle_V = \frac{1}{15N\pi}\sqrt{\frac{12Vc}{kT}}\left(\lambda^2 - \frac{1}{\lambda}\right) \tag{5}$$

We conducted a series of experiments on partially deuterated *cis*-1,4-poly(butadiene) networks in order to investigate the temperature dependence of the NMR line splitting. At each temperature it was allowed 30 min time to stabilize the temperature over the network while the temperature increase was 1 deg per 3 min. The deformation was kept constant at a deformation ratio of 1.48 over a temperature range from −10 to +60 °C.

The splitting, at each temperature, is determined using the two maximum points of the deuterium NMR spectrum. Figure 1 illustrates a spectrum obtained at 27 °C and at the same deformation ratio. The lines are narrow enough to estimate the splittings with an error of 5%.

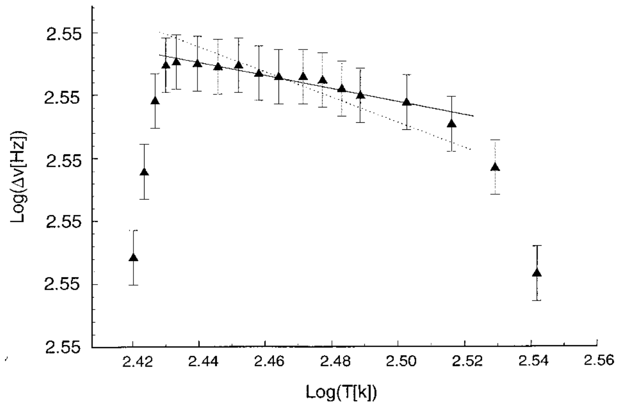

Figure 2. Temperature dependence of deuterium NMR line splitting ($\Delta\nu$) obtained from partially deuterated unfilled *cis*-1,4-poly(butadiene) at a deformation ratio of $\lambda = 1.48$. The straight line corresponds to a least-squares fit with $\log(\Delta\nu) = 3.8 - 0.5 \log(T)$, error bars 5%. The dotted line corresponds to the prediction of Deloche et al. (eq 3).

The results are shown as a logarithmic plot in Figure 2. At the higher temperatures the sample slips out of the grips, and at the lower temperatures the sample crystallizes and doing so breaks. A least-squares fit of the data give a slope of 0.5 ± 0.02, which is in good agreement with the theoretical predictions.

This gives evidence to the temperature dependence of the line splitting; i.e., the NMR line splitting depends on the temperature according to $1/\sqrt{T}$ (see eq 5).

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