Cross-Link Fluctuations and the NMR Properties of Strained Poly(dimethylsiloxane) Networks

M. G. Brereton

IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, U.K.

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ABSTRACT: The doublet structure observed in the ^{2}H NMR spectra of deformed poly(dimethylsiloxane) (PDMS) networks is interpreted in this paper in terms of strain-dependent cross-link fluctuations. Previously this feature has been used as evidence for an orientation-induced weak nematic network ordering. From the experimental results the magnitude of the junction fluctuations in the undeformed state is estimated to be approximately $^1/_3$ of the phantom network result. Using a theory developed by Flory, these restricted junction fluctuations can be related to the elastic properties of the network. In particular, they were related to the deviations of the elastic modulus from the phantom chain result. When expressed in terms of the Mooney–Rivlin constants C_1 and C_2, the Flory theory, together with the deduced value of the junction fluctuations obtained from the NMR results, gives $C_2/C_1 = 0.18$. Using literature data, this value is in close agreement with the value $C_2/C_1 = 0.21$ obtained from mechanical measurements on almost identical networks.

1. Introduction

Deuterium nuclear magnetic resonance (^{2}H NMR) has been extensively used to study the orientational order induced in deformed rubber networks.[1-5] The experimental results of Deloche and Sotta[5] on uniaxially deformed poly(dimethylsiloxane) (PDMS) networks are particularly relevent to this paper. They show that in the undeformed network state the perturbation of the Zeeman levels, by the nuclear quadrapolar interaction, is not completely averaged out by the molecular motion and the levels are broad compared to a liquidlike response. However, the most interesting feature of this work is the well-defined doublet structure that appears immediately after the network is deformed. This is shown by Sotta and Deloche to be inconsistent with a description of the network based on noninteracting chains, i.e., the phantom chain network. Instead they interpret their experimental results in terms of a short-range orientational interaction between the polymer chain segments, which leads to a uniaxial component of the molecular motion about the external force direction. The doublet splitting is shown to be proportional to

$$\nu_Q U(\lambda^2 - 1/\lambda)/N$$

where ν_Q is the quadrapolar coupling constant, U is a new parameter, introduced by Sotta and Deloche, to describe the strength of the orientational field, λ is the deformation ratio in a uniaxial extension, and N is the number of chain segments between cross-link points.

It is the object of this paper to suggest an alternative explanation for the appearance of the doublet structure in the ^{2}H NMR spectra in terms of strain-dependent network junction fluctuations. Flory[6] used this idea in order to account for the deviations of the observed elastic properties of networks from the predictions of the phantom chain. Flory argued that the presence of real impenetrable chains (entanglements) would impede the fluctuations of the cross-link points. This is in contrast to the original phantom chain model for rubber elasticity originally proposed by James and Guth,[7] where the junction points fluctuate in a volume which is independent of the state of strain and of the same order as the size of the chains between the cross-links. Only the mean positions of the junction points deform affinely, and hence the actual chains are nonaffinely deformed. In other theories[8] of rubber elasticity the network junction points are fixed in the material of which they are a part and do not fluctuate. The end-to-end vectors of the chains connecting the junctions are then constrained to deform affinely with the macroscopic strain.

The elastic moduli predicted by these models differ from each other by a factor of 2, with the fully affine model (fixed cross-link points) giving the greater modulus. Flory's idea was to allow the size of the cross-link fluctuations to be strain dependent in such a manner that in a uniaxial extension the fluctuations increased in the direction of the strain. This leads to a transition from an affine to a nonaffine chain deformation as the strain is increased. The subsequent deviations from the phantom chain model were shown by Flory to be consistent with the phenomenological Mooney–Rivlin[9] description.

In this paper it will be shown that strain-dependent cross-link fluctuations can also give rise to a doublet structure in the NMR spectra of exactly the same form as that found by Sotta and Deloche. The main result derived in this paper is the demonstration that the orientational field parameter U of Sotta is replaced by the ratio

$$U/5 \sim 3\langle \Delta \mathbf{R}_0^2 \rangle / 2Nb^2 \qquad (1)$$

where $\langle \Delta \mathbf{R}_0^2 \rangle$ is the average junction fluctuation in the undeformed network state and Nb^2 the mean-square end-to-end distance of the ideal chain of N statistical segments of average length b.

Sotta and Deloche needed a value $U \sim 0.5$ to fit their experimental NMR. By adopting the interpretation proposed in this paper and quantified by (1), this value of U would lead to an estimate of the junction fluctuations $\langle \Delta \mathbf{R}_0^2 \rangle$ as

$$\langle \Delta \mathbf{R}_0^2 \rangle \sim (1/15)Nb^2$$

indicating that the cross-links are closely localized in the network. In section 4 this estimate of $\langle \Delta \mathbf{R}_0^2 \rangle$ is used in a quantitative way to predict, on the basis of the Flory theory, the departure of the elastic modulus of the PDMS network from the phantom chain model result. It will be shown that there is good agreement with literature data on the mechanical properties of similar PDMS networks.

In the next section a scale invariant model for both the NMR interactions (dipole, quadrapole) and the network chains with fluctuating cross-link points is introduced and the transverse NMR properties are evaluated.

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2. Deformed Network Model

The model is shown in Figure 1. The chain between the cross-link points is considered to be composed of N statistical segments $\{b_j\}$, each of average length b. For simplicity a simple uniaxial deformation λ in the direction of the applied field (z direction) will be considered. The instantaneous vector $\mathbf{R}(\lambda;t)$ joining two particular cross-link points can be expressed as

$$\mathbf{R}(\lambda;t) = \bar{\mathbf{R}}(\lambda) + \delta\mathbf{R}(\lambda;t) \tag{2}$$

where $\bar{\mathbf{R}}(\lambda)$ is the mean vector distance between junctions and $\delta\mathbf{R}(\lambda;t)$ describes the strain-dependent fluctuations of the junction points about the mean positions. $\bar{\mathbf{R}}(\lambda)$ is assumed to deform affinely with the macroscopic strain so that

$$\bar{\mathbf{R}}(\lambda) = \lambda\cdot\bar{\mathbf{R}}_0 \tag{3}$$

λ is a diagonal matrix with elements $(\lambda, \lambda^{-1/2}, \lambda^{-1/2})$ for a volume preserving uniaxial extension, and $\bar{\mathbf{R}}_0$ is the mean vector distance between junctions in the undeformed state. In the model suggested by Flory[8] the junction fluctuations $\Delta\bar{\mathbf{R}}(\lambda;t)$ are allowed to be strain dependent. There is no a priori reason why they should also be affine in the deformation; however, for small deformations this is clearly the simplest choice and the one that is ultimately confirmed by the experimental results. Set

$$\delta\mathbf{R}(\lambda;t) = \lambda\cdot\Delta\mathbf{R}_0(t) \tag{4}$$

In the next section the NMR properties of this model are considered.

3. Network NMR Properties

When details about the dynamics of the monomeric units can be completely ignored, the NMR properties can be transferred to a coarse scale described in terms of statistical bond vectors $\{\mathbf{b}_j\}$. This approach was pioneered by Cohen-Addad.[10-12] If the dynamics of the semilocal, statistical vectors $\{\mathbf{b}_j\}$ are also fast, then the process can be continued[13] and the NMR properties are further rescaled to a space scale determined by the end-to-end vector $\mathbf{R}$. At this scale the dipolar interactions lead to a relaxation of transverse magnetization $M_+(t)$ given by

$$M_+(t) = M_0\left\langle \cos\frac{3\nu}{2N}\int_0^t \frac{\{2Z^2(\lambda;t') - X^2(\lambda;t') - Y^2(\lambda;t')\}}{Nb^2}\,dt' \right\rangle \tag{5}$$

$X(\lambda;t)$, $Y(\lambda,t)$, and $Z(\lambda,t)$ are the coordinates of the chain end-to-end vector $\mathbf{R}(\lambda;t)$ with the other end set at the origin. ν is a rescaled dipolar interaction constant, and N is the number of statistical vectors $\{\mathbf{b}_j\}$ comprising the chain between cross-link points. The same form of results holds for quadrapolar interactions when the asymmetry parameter can be neglected. A full account of the use of ^{2}H NMR in oriented systems has been given by Samulski.[14] The advantage of the repeated rescaling is that the coordinates (X,Y,Z) may be treated as independent Gaussian random variables and hence the mathematical problem is completely posed by the term

$$g(\nu,t) = \left\langle \exp\left(\frac{3\nu i}{2N}\right)\int_0^t \frac{X^2(t')}{Nb^2}\,dt' \right\rangle = \langle g\{\nu,t;X(\lambda;t)\}\rangle \tag{6}$$

Then the normalized relaxation function $G(t) = M_+(t)/M_0$ is given by

$$G(t) = \text{real part}\,[g(2\nu,t)\;\; g(-\nu,t)\;\; g(-\nu,t)] \tag{7}$$

For a network with fluctuating cross-links, set $X(\lambda,t) = \bar{X}(\lambda) + \delta X(\lambda;t)$ in (6) for $g\{\nu,t;X(\lambda;t)\}$ to give

$$g\{\nu,t;X(\lambda;t)\} = \exp\left(\frac{3\nu i}{2N}\frac{1}{Nb^2}\right)[\bar{X}^2(\lambda)\,t + 2\bar{X}(\lambda)\int_0^t \delta X(\lambda;t')\,dt' + \int_0^t \delta X^2(\lambda,t')\,dt'] \tag{8}$$

The averaging in (6) now requires a dynamical averaging over the cross-link fluctuations $\delta X(\lambda;t')$ and a static average over the mean distance between cross-links $\bar{X}$. In principle, the junction fluctuations $\delta X(t')$ will be governed by some dynamical model. For the case where the fluctuations are correlated by a single relaxation time, i.e.

$$\langle \delta X(0)\,\delta X(t)\rangle = \langle \delta X^2\rangle \exp(-t/\tau)$$

an exact solution is possible and will be reported on elsewhere. For the purpose of this paper it will be assumed that the dynamics are fast so that only instantaneous values of $\delta X(t)$ are required. Since these are assumed to be Gaussian random variables, the average of (8) over the fluctuations can be directly evaluated to give

$$g(\nu,t;\bar{X}) = \langle g\{\nu,t;X(\lambda;t)\}\rangle_{\{\delta X\}} = \exp\left(\frac{3\nu i}{2N}\frac{1}{Nb^2}\right)[\bar{X}^2(\lambda)\,t + \langle \delta X^2(\lambda)\rangle t] \tag{9}$$

The full relaxation function $G(t;\bar{X})$ for a particular chain, where the mean direction between the cross-link points is $\bar{\mathbf{R}}$, is now given from (7), using (9), as

$$G(t;\bar{\mathbf{R}}) = \text{real part}\,\{g(2\nu,t;\bar{Z})\;\; g(-\nu,t;\bar{X})\;\; g(-\nu,t;\bar{Y})\} = \cos\Delta(\bar{\mathbf{R}})t$$

where

$$\Delta(\bar{\mathbf{R}}) = \frac{\nu}{N}\frac{3}{2Nb^2}[\{2\bar{Z}^2 - \bar{X}^2 - \bar{Y}^2\} - \{2\langle \delta Z^2\rangle - \langle \delta X^2\rangle - \langle \delta Y^2\rangle\}] = \frac{\nu}{N}\left[3\frac{\bar{\mathbf{R}}^2}{Nb^2}P_2(\bar{\vartheta}) + \frac{\langle \delta\mathbf{R}_0^2\rangle}{Nb^2}\{\lambda^2 - 1\}\right] \tag{10}$$

$P_2(\bar{\vartheta})$ is the second Legendre polynomial and $\bar{\vartheta}$ the angle between $\bar{\mathbf{R}}$ and the applied field. For the general case where the anisotropy of the junction fluctuation vector $\delta\mathbf{R}(\lambda;t)$ is not parallel to the NMR magnetic field $\mathbf{B}$ but is at an angle Ω, the second term in (10) becomes

$$\frac{\langle \delta\mathbf{R}_0^2\rangle}{Nb^2}\left\{\lambda^2 - \frac{1}{\lambda}\right\}P_2(\Omega)$$

The assumption that the fluctuations $\langle \delta Z^2\rangle$, $\langle \delta X^2\rangle$, and $\langle \delta Y^2\rangle$ deform affinely (eq 4) has been used and in the undeformed state $\langle \delta Z^2\rangle = \langle \Delta\mathbf{R}^2\rangle/3$, etc. The discussion so far has been confined to a single network chain, and the final step is to average the relaxation function $G(t;\bar{\mathbf{R}})$ over the static distribution of the network vectors $\bar{\mathbf{R}}(\lambda)$ which are assumed to be gaussianly distributed.

$$H(\bar{\mathbf{R}}) \sim \exp[-3\bar{\mathbf{R}}^2/(2\langle \bar{\mathbf{R}}^2\rangle)]$$

Then

$$G(t) = \int d\mathbf{R}\, H(\bar{\mathbf{R}})\, G(t;\bar{\mathbf{R}}) = \int d\mathbf{R}\, H(\bar{\mathbf{R}}) \cos\Delta(\bar{\mathbf{R}})t \tag{11}$$

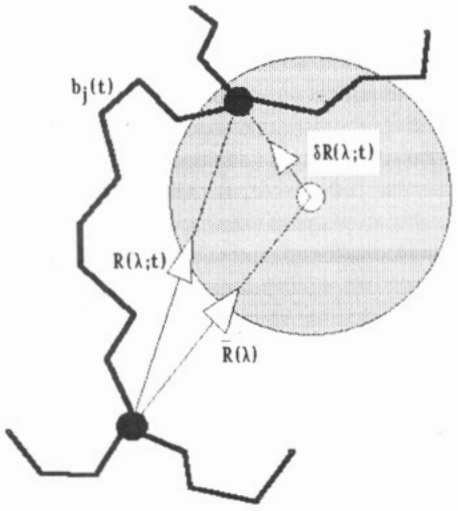

Figure 1. Cross-link fluctuation volume shown as the shaded area. $\bar{\mathbf{R}}(\lambda)$ is the mean vector distance between cross-links and $\delta\mathbf{R}(\lambda;t)$ the instantaneous fluctuation.

This expression can be compared with the corresponding one from the work of Sotta and Deloche which is written as

$$G(t) = \int d\mathbf{R}\, h(\mathbf{R})\, e^{-t/T_2} \cos \Delta_R t \qquad (12)$$

$h(\mathbf{R})$ is the distribution function of the complete chain end-to-end vectors $\mathbf{R}$. T_2 is the usual NMR relaxation time related to the molecular motion. Δ_R is the residual quadrapolar interaction term, given by Sotta and Deloche as

$$\Delta_R = \frac{\nu_Q}{5N}\left[3\frac{\mathbf{R}^2}{Nb^2}P_2(\vartheta) + \frac{2}{3}\frac{U}{(5-U)}(\lambda^2 - 1/\lambda)P_2(\Omega)\right] \qquad (13)$$

ν_Q is the quadrapolar coupling constant and U characterizes the strength of the orientational field postulated by Sotta and Deloche.

The work presented in this paper has been in the limit of very fast molecular dynamics and consequently the T_2 term is absent in the result (eq 11). The residual quadrapolar interaction derived from the assumption of strain-dependent junction fluctuations is given by (10), which is very similar in form to that given by Sotta and Deloche (eq 13). The first term in the expression of Sotta and Deloche comes from averaging the quadrapolar interaction along the complete chain end-to-end vector $\mathbf{R}$, whereas in the present work the first term comes from averaging along the mean (static) vector distance $\bar{\mathbf{R}}$ between two cross-link points. The second term in the present result (eq 10) represents the averaging of the quadrapolar interaction over the dynamic fluctuations of the cross-link points. The essential point in this work is that these must be anisotropically strain dependent if this is not to average to zero. The second term can be compared with the corresponding one of Sotta and Deloche if the orientational field parameter U and junction fluctuations $\langle\Delta\mathbf{R}_0^2\rangle$ are identified by

$$\frac{\langle\Delta\mathbf{R}_0^2\rangle}{Nb^2} \equiv \frac{2}{3}\frac{U}{(5-U)} \qquad (14)$$

Sotta and Deloche report that the qualitative features of the doublet structure seen in the NMR spectra of end-linked PDMS chains are fitted by adjusting $U \sim 0.5$. By adoption of the alternative explanation proposed in this paper, this implies that the junction fluctuations $\langle\Delta\mathbf{R}_0^2\rangle$ in the undeformed network PDMS are $\sim 1/15$ of the mean-square chain length.

In the next section the effect of the restricted junction fluctuations on the elastic properties of the PDMS network is discussed on the basis of Flory's theory.

4. Mechanical Properties

In a phantom network of functionality φ the junction fluctuations ΔR_{ph}^2 are given by[8]

$$\Delta R_{ph}^2 = \frac{(\varphi-1)}{\varphi(\varphi-2)}Nb^2 \qquad (15)$$

The PDMS networks used by Sotta and Deloche were hexafunctional ($\varphi = 6$) and hence $\Delta R_{ph}^2 \sim Nb^2/5$. From the reinterpretation of the NMR data given in this paper the actual junction fluctuations $\langle\delta\mathbf{R}_0^2\rangle$ are $Nb^2/15$, i.e., a factor 3 smaller. In the theory of Flory this reduction of junction fluctuations is assigned to entanglements and the subsequent effect on the mechanical properties of the network is written in terms of the tensile force f for a simple elongation as

$$f = f_{ph} + f_e \qquad (16)$$

where f_{ph} is the phantom chain result with junction fluctuations ΔR_{ph}^2 independent of the applied strain and f_e arises from junction fluctuations $\Delta s(\lambda)^2$, which are restricted solely by entanglements and considered to be affinely strain dependent, i.e., $\Delta S(\lambda) = \lambda\cdot\Delta s_0$. The actual junction fluctuations $\delta\mathbf{R}(\lambda)^2$ used in this paper are related to the separate fluctuation terms ΔX_{ph}^2 and $\Delta s(\lambda)^2$ by an expression given by Flory. In component form this can be written as, e.g.

$$\frac{1}{\delta X(\lambda)} = \frac{1}{\Delta X_{ph}} + \frac{1}{\Delta s(\lambda)} \qquad (17)$$

If $\delta X(\lambda) \ll \Delta X_{ph}$, then $\delta X(\lambda) \sim \Delta s(\lambda)$, which is affine in the strain and was the result used in section 2. However, it might be objected that the estimate $\Delta X(\lambda) \sim \Delta X_{ph}/3$ does not strongly satisfy this criterion. Nevertheless, the replacement $\delta X(\lambda) \sim \Delta s(\lambda)$ is justified because the required combination (eq 10) of these fluctuations has the form $(2\delta Z^2 - \delta X^2 - \delta Y^2)$ so that the leading term for small deformations is $2\Delta s_0(\lambda^2 - 1/\lambda)/3$.

The expression developed by Flory for the entanglement contribution, f_e, and hence f is highly nonlinear in the deformation ratio λ but is qualitatively similar to the phenomenological Mooney–Rivlin form

$$f = (2C_1/L_0)(\lambda - \lambda^{-2}) + (2C_2/L_0)(1 - \lambda^{-3}) \qquad (18)$$

where C_1 and C_2 are constants and L_0 is the undeformed length of the sample. The ratio C_2/C_1 of the Mooney–Rivlin constants can be identified as

$$\frac{C_2}{C_1} = \left.\frac{f_e}{f_{ph}}\right|_{\lambda=1} \qquad (19)$$

where f_{ph} is the first term and f_e the second term of (18). In the limit $\lambda \to 1$ the expressions given by Flory for f_e and f_{ph} reduce to give the following result:

$$\left.\frac{f_e}{f_{ph}}\right|_{\lambda=1} = \frac{2}{\varphi-2}\frac{\kappa^2(1+\kappa^2)}{(1+\kappa)^4} = \frac{C_2}{C_1} \qquad (20)$$

κ is the principal parameter of the model, given by the ratio of the phantom network cross-link fluctuations to

the entangled network fluctuations:

$$\kappa = \frac{\Delta R_{ph}^2}{\Delta s_0^2} = \frac{\varphi - 1}{\varphi(\varphi - 2)} \frac{Nb^2}{\Delta s_0^2} \tag{21}$$

Using the value $\Delta s_0^2 \sim Nb^2/15$ derived from the NMR results and $\varphi = 6$ in (21) gives $\kappa = 25/8 = 3.125$. Consequently, from the Flory model, i.e., expression (20)

$$\left.\frac{f_e}{f_{ph}}\right|_{\lambda=1} = 0.18 = \frac{C_2}{C_1} \tag{22}$$

In the literature Mark et al.[15] have measured this ratio for hexafunctional networks of $M_n = 11\,300$ and found the value

$$C_2/C_1 = 0.21 \tag{23}$$

For the shorter chains used by Sotta and Deloche ($M_n = 9700$) this ratio is expected to be slightly lower. In any case the agreement is excellent and together with the Flory theory clearly supports the interpretation of the doublet structure in the NMR spectra as arising from network junction fluctuations.

5. Conclusions

The doublet structure observed by Sotta and Deloche in the ^2H NMR spectra of deformed PDMS networks has been interpreted by these workers and others in terms of a weak nematic ordering. For this purpose they introduce an orientational mean-field parameter U. This work confirms that there is no doublet splitting for a phantom chain network where the junction fluctuations remain isotropic in the deformed state or where they are fixed in the material and do not fluctuate. However, if part of the fluctuations is allowed to be strain dependent, then the doublet splitting can occur and the form is similar to that proposed by Sotta and Deloche, except that the mean-field parameter U is redundant and is replaced by

$$U/5 \sim 3\langle \Delta \mathbf{R}_0^2 \rangle / 2Nb^2$$

Using the value $U = 0.1$ chosen by Sotta and Deloche to fit their results gives the size of the junction fluctuations in the undeformed state as $\langle \Delta \mathbf{R}_0^2 \rangle Nb^2/15$. These fluctuations are approximately a factor of 3 times more restricted than the phantom chain junctions. Using a theory developed by Flory, these restricted junction fluctuations can be related to the elastic properties of the network. In particular, they relate to the deviations of the modulus from the phantom chain result. When expressed in terms of the Mooney–Rivlin constants C_1 and C_2, the Flory theory gives $C_2/C_1 = 0.18$, using the deduced value of $\langle \Delta \mathbf{R}_0^2 \rangle$ from the NMR results. This value is in close agreement with the value $C_2/C_1 = 0.21$ taken from the literature on almost identical networks.

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