1152 *Macromolecules* **1993,** *26,* 1152–1157

NMR Study of the Molecular Anisotropy Induced in a Strained Rubber Network

M. G. Brereton

Interdisiplinary Research Centre in Polymer Science and Technology, Department of Physics, The University of Leeds, Leeds LS2 9JT, U.K.

Received September 8, 1992; Revised Manuscript Received November 6, 1992

ABSTRACT: The splitting seen in the NMR line shape obtained from deformed networks has been cited as evidence of short-range orientational interactions between segments belonging to different chains. In this paper, it is shown that a splitting can still occur when only the usual short-range and isotropic excluded-volume interactions are acting. The orientational effects are shown to originate from the anisotropic screening properties of the deformed network chains.

1. Introduction

Deuterium NMR gives direct access to the anisotropy of molecular motion and has been used in both network chains[1] and free chains dissolved in the network.[2] The experimental results are quite unambiguous: In the undeformed state the spectrum is a single line characteristic of a liquid. When the network is uniaxially deformed by an amount λ, a well-defined doublet structure appears where the splitting $\Delta\nu$ varies linearly with $(\lambda^2 - \lambda^{-1})$. The magnitude is the same for both the network chains and the free chains of comparable length dissolved in the network; i.e., the effect is not directly dependent on the presence of the cross-links or entanglements.

The possibilities for interpreting this result are limited since for noninteracting Gaussian network chains it has already been shown[1] that the deformation anisotropy transmitted to the network chains through the cross-links only alters the line shape and does not give rise to a doublet structure. The conclusion is that the observed splitting must primarily be due to the interactions between the chains. The splitting of NMR lines is a well-known phenomenon in liquid crystal systems, and on the basis of the work of Jarry and Monnerie,[3] nematic couplings between chain segments have also been evoked[1,4,5] to explain the polymer results. These have the orientational dependent form:

$$W(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta}) \approx -u(3\cos^2\vartheta_{ij} - 1)/2 \qquad (1.1)$$

where ϑ_{ij} is the angle between a segment on the α chain at $\mathbf{r}_i^{\alpha}$ and another on the β chain at $\mathbf{r}_j^{\beta}$. Such interactions would certainly make the system responsive to a uniaxial strain but would also imply that the system could spontaneously order at some temperature. The splitting of the NMR line is seen for polymers which are not normally regarded as nematic.

An alternative explanation has been given in ref 6, where it was shown that a line splitting would occur if the network junction fluctuations became anisotropic under a deformation. In this work, the explanation based on segment–segment interactions will be closely examined. It will be shown that the nematic assumption is not necessary and that the usual short-range and isotropic excluded-volume interactions between segments, i.e.

$$W(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta}) \sim \delta(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta}) \qquad (1.2)$$

are sufficient to explain the NMR line splitting. The novel feature of the present work is that an account will be taken of the modified screening properties of network chains when they are deformed. The situation is similar in some respects to the melt, where an effective attractive interaction between segments is induced by the density fluctuations.[6] This is isotropic and acts so as to screen the direct repulsive excluded-volume interaction. Density fluctuations also exist in network systems but with significant differences associated with the loss of translational freedom of the chains quenched in the network by the cross-links. Methods for dealing with this aspect of the problem have been developed in ref 7. There it was shown that, despite the restriction on the center of mass motion, the density fluctuations on the scale of a single chain are very similar to those acting in the melt. Equally important is the fact that the network density fluctuations associated with a particular wave vector depend on the orientation of this vector with respect to the deformation. The resulting screened interaction will be shown to have an additional dipolar term which leads directly to the observed line splitting.

In this paper, the principal results will be established for a one-component network. In a subsequent paper, the more general case of a blend of network chains of type A with free chains of type B will be considered together with a similar situation presented by interpenetrating polymer networks. The presence of a Flory interaction parameter in these systems will be shown to greatly enhance the range of NMR behavior.

2. NMR Model

The basic model to describe the NMR properties is shown in Figure 1. It consists of a single strand of polymer chain between two network junction points. The configuration of the chain will be described in terms of N statistical segment bond vectors $\{\mathbf{b}_i\}$. Each chain is considered to carry a NMR-active bond $\mathbf{b}_j$. At the atomic level this will consist of either a proton spin pair interacting with each other through a dipolar interaction or a deuterium quadrupole interacting with an electric field gradient at the nucleus.[4] At the semilocal level described by the statistical bond vectors $\{\mathbf{b}_i\}$, the perturbation of the Zeeman levels of the relevant nuclear spin is sensitive to the orientation of this bond through the interaction term (expressed in frequency units)

$$\begin{aligned}\epsilon\{\mathbf{b}_j\} &= \nu_{\mathrm{o}}\{3\cos^2\alpha_j(t) - 1\} \\ &\approx \nu_{\mathrm{o}}(2b_{jz}^{\ 2} - b_{jx}^{\ 2} - b_{jy}^{\ 2})/b^2 \qquad (2.1)\end{aligned}$$

ν_{o} is an interaction constant, b is the average length of the jth bond vector with components b_{jx}, b_{jy}, and b_{jz}, and $\alpha_j(t)$ is the angle the bond makes to the applied magnetic field along the z axis. This interaction causes a dephasing of

0024-9297/93/2226-1152$04.00/0

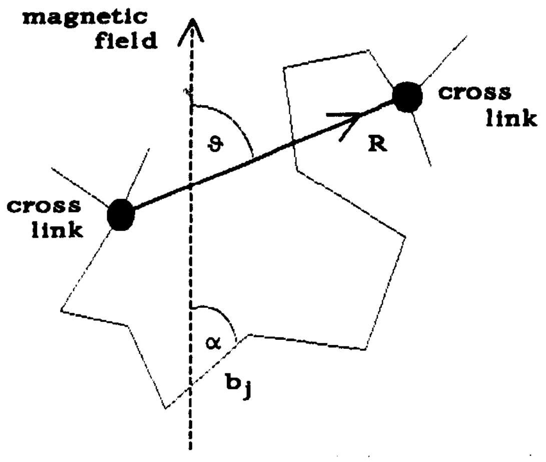

Figure 1. The NMR-active bond $\mathbf{b}_j$: part of a chain of N bonds between two cross-link points a vector distance $\mathbf{R}$ apart.

the transverse components $M_+(t)$ of the nuclear magnetization. When the bond vector dynamics are fast compared to the time set by ν_0^{-1} the subsequent relaxation of magnetization is described by[4]

$$M_+(t)/M_+(0) = G(t;\mathbf{b}_j) = \cos\{\langle\epsilon(\mathbf{b}_j)\rangle t\} \qquad (2.2)$$

where the averaging $\langle\cdots\rangle$ is over all states accessible to the bond vector together with the usual Boltzmann weighting. If the bond can completely reorient then $\langle b_z^2\rangle = \langle b_x^2\rangle = \langle b_y^2\rangle$ and the interaction energy $\epsilon\{\mathbf{b}_j\}$ is averaged to zero.

For the systems of interest in this paper there are two factors which hinder the complete reorientation of the bond vector $\mathbf{b}_j$ and introduce an anisotropy dependent on the state of deformation of the network. First, the network junction points restrict the chain end to end vector $\mathbf{r}_n$ to the fixed vector distance $\mathbf{R}$ between the links. This constrains the bond vectors so that

$$\sum_{i=1}^{N} \mathbf{b}_i = \mathbf{R}$$

Second, there will be an interaction W between these chain segments and the rest of the deformed network. At this stage the form of W does not need to be specified and could include both nematic and excluded-volume interactions. In the statistical mechanical calculation of the interaction energy $\langle\epsilon(\mathbf{b}_j)\rangle$, the constraint is handled by means of a delta function $\delta(\sum b_i - R)$ and the interaction W by the usual Boltzmann factor.

$$\langle\epsilon\{\mathbf{b}_j\}\rangle = \frac{\langle\epsilon\{\mathbf{b}_j\}\delta(\sum b_i - R)\exp(-W/kT)\rangle_0}{\langle\delta(\sum b_i - R)\exp(-W/kT)\rangle_0} \qquad (2.3)$$

where $\langle\cdots\rangle_0$ is an average over the unperturbed configurations of all the chains in the network.

Apart from the single chain $\{\mathbf{r}_i\}$ carrying the NMR probe, the coordinates $\{C\} = \{\mathbf{r}_i^{\alpha}\}, \{\mathbf{r}_i^{\beta}\}, \cdots$ of all the other network chains only occur in the interaction energy W: The effect of averaging over all these other chains is to replace W/kT by a screened effective interaction V^* according to

$$\langle\exp(-W/kT)\rangle_{\{C\}} = \exp(-\mathrm{V}^*) \qquad (2.4)$$

where V^* depends only on the coordinates of the single chain carrying the NMR bond under consideration; i.e.

$$V^* = \sum_{ij} V^*(\mathbf{r}_i - \mathbf{r}_j)$$

The details of this calculation will be discussed later when an explicit form for V^* will be presented. This is not actually required at the moment except to comment that because the potential V^* is screened it can be treated by perturbation theory. To first order, the NMR interaction energy is given from eq 2.3 as

$$\begin{aligned}\langle\epsilon\{\mathbf{b}_j\}\rangle &= \frac{\langle\epsilon\{\mathbf{b}_j\}\delta(\sum b_i - R)(1 - V^*)\rangle_0}{\langle\delta(\sum b_i - R)(1 - V^*)\rangle_0} \\ &= \langle\epsilon\{\mathbf{b}_j\}\rangle_R - \{\langle\epsilon\{\mathbf{b}_j\}V^*\rangle_R - \langle\epsilon\{\mathbf{b}_j\}\rangle_R\langle V^*\rangle_R\} \qquad (2.5)\end{aligned}$$

where $\langle\cdots\rangle_R$ is a short notation for the constrained single chain average

$$\langle\cdots\rangle_R = \frac{\langle\cdots\delta(\sum b_i - R)\rangle_0}{\langle\delta(\sum b_i - R)\rangle_0}$$

It will be shown in the next two sections that the effects of the constraint $\sum\mathbf{b}_i = \mathbf{R}$ and the screened potential V^* on the interaction energy $\langle\epsilon\{\mathbf{b}_j\}\rangle$ are both of the order N^{-1}. Hence, in the second group of terms in eq 2.5 the constraint can be ignored and the last term vanishes since $\langle\epsilon\{\mathbf{b}_j\}\rangle_0 = 0$. The interaction energy is then given by

$$\langle\epsilon\{\mathbf{b}_j\}\rangle = \langle\epsilon\{\mathbf{b}_j\}\rangle_R - \langle\epsilon\{\mathbf{b}_j\}V^*\rangle_0 \qquad (2.6)$$

The anisotropy of the NMR interaction energy due to the network junction constraint is contained in the term $\langle\epsilon\{\mathbf{b}_j\}\rangle_R$, while that due to the interactions is contained in the term $\langle\epsilon\{\mathbf{b}_j\}V^*\rangle_0$. The junction term will be considered in the next section, where it will be shown that it affects the NMR line width but does *not* lead to a line splitting. In section 4 the splitting will be shown to arise from isotropic excluded-volume interactions.

3. Anisotropy of the NMR Interaction Energy Due to Network Junctions

In this section the contribution of the network junction constraints to the NMR relaxation function in the absence of segment interactions will be discussed, i.e., the term

$$G_0(t;R) = \cos\{\langle\epsilon(\mathbf{b}_j)\rangle_R t\} \qquad (3.1)$$

The effect that the end to end constraint has on this quantity can be seen directly from eq 2.1, where the interaction energy is related to the size of the bond vector $\mathbf{b}_j^2$. The result for $\langle\mathbf{b}_j^2\rangle_R$ is well-known[8] and given in component form by

$$\langle\mathbf{b}_{xj}^2\rangle_R = b^2/3 + X^2/N^2 \qquad (3.2)$$

and similarly for b_y and b_z, where $\mathbf{R} = X, Y, Z$ and is dependent on the macroscopic deformation applied to the system. Hence, in the absence of any interaction terms, the constrained NMR interaction energy is given as

$$\begin{aligned}\langle\epsilon\{\mathbf{b}_j\}\rangle_R &= \frac{\nu_0}{N}\left(\frac{2Z^2 - X^2 - Y^2}{Nb^2}\right) \\ &\approx \frac{\nu_0}{N}\{3\cos^2\vartheta - 1\} \qquad (3.3)\end{aligned}$$

This result is well-know[9] and is a rescaled version of the original expression (eq 2.1). The interaction strength ν_0 is reduced by N, and $\langle\epsilon\{\mathbf{b}_j\}\rangle_R$ now depends on the angle ϑ between the vector $\mathbf{R}$ and the applied magnetic field instead of the angle α between the bond $\mathbf{b}_j$ and the field.

The NMR line shape is given by the Fourier transform $G_0(\omega;R)$

$$G_0(\omega;R) = \int \mathrm{d}t\, \exp(i\omega t)\, G_0(t;R) \qquad (3.4)$$

Using eq 3.1 for $G_0(t;R)$, $G_0(\omega;R)$ is seen to consist of two

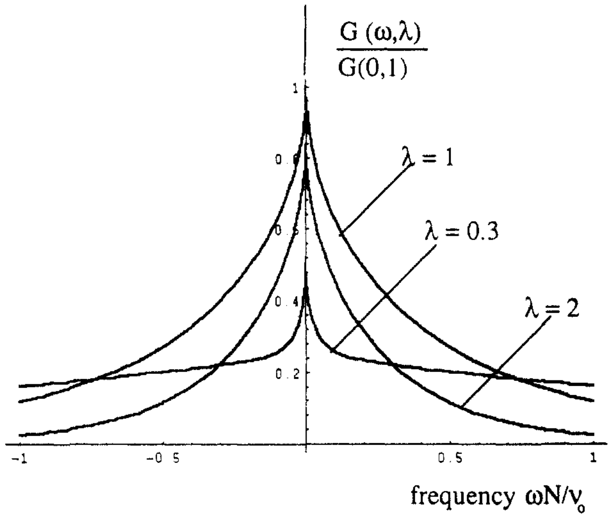

Figure 2. Effect of a uniaxial deformation λ on the NMR relaxation function given by eq 3.8, in the absence of segment interactions.

components at $\omega = \pm\langle\epsilon\{\mathbf{b}_j\}\rangle_R$

$$G_o(\omega;\mathbf{R}) = \pi\{\delta(\omega + \langle\epsilon\{\mathbf{b}_j\}\rangle_R) + \delta(\omega - \langle\epsilon\{\mathbf{b}_j\}\rangle_R)\} \quad (3.5)$$

Thus, for a single chain the network constraint on the end to end vector $\mathbf{r}_n = \mathbf{R}$ does lead to a line splitting. However, the orientation of the deformed network vectors $\{\mathbf{R}\}$ is distributed in space and $G(t,\mathbf{R})$ or equivalently $G_o(\omega;\mathbf{R})$ must be averaged over the $\{\mathbf{R}\}$. To accomplish this the affine deformation assumption is made whereby $\mathbf{R}$ is related to the undeformed network vector $\mathbf{R}_o$ by

$$\mathbf{R} = \lambda\cdot\mathbf{R}_o \quad (3.6)$$

The $\mathbf{R}_o$ are then assumed to be Gaussianly distributed so that the measured relaxation function in either the time or frequency domain is given by

$$\left.\begin{matrix} G(t;\lambda) \\ G(\omega;\lambda) \end{matrix}\right\} = \int \mathrm{d}^3R_o\, P(R_o) \left\{\begin{matrix} G(t;\lambda\cdot\mathbf{R}_o) \\ G(\omega;\lambda\cdot\mathbf{R}_o) \end{matrix}\right.$$

$$\text{where} \quad P(R_o) = (2\pi Nb^2/3)^{-3/2} \exp(-3R_o^{\,2}/2NB^2) \quad (3.7)$$

$G_o(t;\lambda)$ can be evaluated analytically as well as the Fourier transform $G(\omega;\lambda)$. While $G_o(t;\lambda)$ is well-known in the literature,[10] $G_o(\omega;\lambda)$ does not seem to be quoted. The result is given in Appendix 1, where it is shown that $G_o(\omega;\lambda)$ can be expressed in terms of the complementary error function erfc. The normalized result can be written as

$$\frac{G_o(\omega;\lambda)}{G_o(0;1)} = \sqrt{\frac{3}{2\lambda + \lambda^{-2}}} \exp(-3\Omega\lambda/2)\{1 + \exp(3\Omega\lambda) \times \operatorname{erfc}(\sqrt{3\Omega(2\lambda + \lambda^{-2})/2})\} \quad (3.8)$$

where Ω is the scaled frequency variable

$$\Omega = N\omega/\nu_o$$

For a uniaxial deformation $G_o(\omega;\lambda)/G_o(0;1)$ is shown in Figure 2 as a function of Ω and λ. It can be seen that the shape of the line changes with deformation but does not show any splitting. The implication of this result is that the NMR line splitting must be due to the intersegment interactions. This is considered in the next section.

4. Anisotropy Due to Segment–Segment Interactions

The second factor preventing a complete reorientation of the NMR bond vector $\mathbf{b}_j$ is the interaction between this unit and the rest of the chain segments in the deformed network. The effect on the NMR interaction energy is given from eq 2.6 by the term $\langle\epsilon V^*\rangle_o$. V^* is a screened potential derived from the direct segment–segment interactions W according to eq 2.4. In previous work screening was not considered and instead, the direct interactions were assumed to have the nematic form (eq 1.1). In this work it will be shown that this assumption is not necessary and for the direct interaction between segments the usual short-range and isotropic excluded-volume interactions will be taken; i.e.

$$W(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta}) = Vb^3\delta(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta}) \quad (4.1)$$

At first sight it is not clear that the screening properties of network chains should be similar to those in the melt, because of the loss of translational freedom by the network chains. In previous work[7] the quenched degree of translational freedom was accounted for by a replica calculation. There it was shown that for long chains the density fluctuations for inverse wave vectors of the size of the chain differ from those in the melt only by terms of the order N^{-1}. For smaller wave vectors there are substantial differences reflecting the loss of translational freedom. In a subsequent paper[11] it was shown that the screening properties of the network chains on the size of a single chain were identical to those in the melt up to terms of the order $N^{-1/2}$. Consequently, in this work the melt result will be used and the Fourier components V_q^* of the screened potential taken from the work of Edwards[12] as

$$V_q^* = \frac{V_q/kT}{1 + V_qS_q^{\,o}/kT} \quad (4.2)$$

V_q is the Fourier transform of the direct interaction, i.e., from the form (eq 4.1) $V_q = Vb^3$ and $S_q^{\,o}$ is the structure factor for noninteracting chains.

One important modification needs to be made to this result in order to introduce deformation into the system. The length of the chains is controlled by coupling an external field μ to the end to end vector $\mathbf{r}_N^{\alpha}$ of each chain α by means of an additional interaction term $\mu\cdot\mathbf{r}_N^{\alpha}$. The effect is that the Edwards result (eq 4.2) holds but that $S_q^{\,o}$ is replaced by $S_q^{\,o}(\mu)$, the structure factor for noninteracting chains in an external field μ defined by

$$S_q^{\,o}(\mu) = \Omega^{-1}\sum_{ij\alpha}\langle\exp(i\mathbf{q}\cdot(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\alpha})) + \mu\cdot\mathbf{r}_N\rangle_o \quad (4.3)$$

The value of μ is adjusted so that

$$\langle\mathbf{r}_N^{\,2}\rangle = Nb^2\{\lambda_x^{\,2} + \lambda_y^{\,2} + \lambda_z^{\,2}\}$$

which determines μ as

$$\mu^2 = \frac{1}{Nb^2}[\{\lambda_x^{\,2} + \lambda_y^{\,2} + \lambda_z^{\,2}\} - 3] \quad (4.4)$$

(the interaction terms can be neglected). The contribution of the screened potential to the NMR interaction energy $\langle\epsilon\rangle$ is given by the unperturbed average:

$$\langle\epsilon\{\mathbf{b}_j(t)\}V^*(\mu)\rangle_o \quad (4.5)$$

where

$$V^*(\mu) = \sum_{mn} V^*(\mathbf{r}_m - \mathbf{r}_n;\mu) = \frac{1}{\Omega}\sum_{mnq} V_q^*(\mu)\exp(i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n))$$

$V_q^*(\mu)$ is given by eq 4.2 with $S_q^{\,o}$ replaced by $S_q^{\,o}(\mu)$. The average $\langle\epsilon\{\mathbf{b}_j(t)\}V^*(\mu)\rangle_o$ can be evaluated without the need of an explicit form for $V_q(\mu)$. The details are given in Appendix 2 and the result, for j far from the end points of the chain, can be written as

$$\langle \epsilon\{\mathbf{b}_j(t)\} V^*(\mu) \rangle_0 = \frac{8\nu_o}{b^2}\int \frac{d^3q}{(2\pi)^3} V_q^*(\mu) \frac{1}{q^4}\{2q_z^2 - q_x^2 - q_y^2\} \tag{4.6}$$

For $\mu = 0$ the potential is rotationally symmetric and $\langle \epsilon V^* \rangle_o = 0$. The asymmetry in V^* is contained in the μ dependent terms, i.e., in the deformed single-chain structure factors $S_q^o(\mu)$. For a Gaussian chain, $S_q^o(\mu)$ is readily evaluated to give

$$S_q^o(\mu) = \frac{12c}{b^2}\frac{1}{q^2 + 4(\mu\cdot\hat{\mathbf{q}})^2} \tag{4.7}$$

where $\hat{\mathbf{q}}$ is the unit vector $\mathbf{q}/|\mathbf{q}|$ and c is the concentration of monomer units. From eq 4.4 it can be seen that μ^2 is of the order of N^{-1} and consequently $V_q^*(\mu)$ need only be expanded up to first order in $(\mu\cdot\hat{\mathbf{q}})^2$. The result can be written as

$$V_q^*(\mu) = V_q^*(0) + (\mu\cdot\hat{\mathbf{q}})^2 f(q^2) \tag{4.8}$$

where based on the explicit forms (4.2) and (4.7)

$$f(q^2) = \frac{b^2}{3c}\left[\frac{V_q S_q^o/kT}{1 + V_q S_q^o/kT}\right]^2 = \frac{b^2}{3c}\left[\frac{\xi^{-2}}{q^2 + \xi^{-2}}\right]^2 \tag{4.9}$$

where ξ is the Edwards screening length

$$\xi = \sqrt{kT/(12cbV)}$$

It is interesting to note that the term $(\mu\cdot\hat{\mathbf{q}})^2$ in the expression (4.8) for V_q^*, when Fourier transformed, gives rise to a dipolar form of spatial dependence of $V^*(R)$:

$$\frac{\mu\cdot\mu - 3(\mu\cdot\hat{\mathbf{R}})^2}{R^3}$$

Finally, using eq 4.8, the contribution of the screened interaction to the NMR interaction energy is given by (the details are given in Appendix 2)

$$\langle \epsilon\{\mathbf{b}_j(t)\} V^*(\mu) \rangle_o = \{2\mu_z^2 - \mu_x^2 - \mu_y^2\}\frac{2\nu_o}{5\pi^2 b^2}\int_0^\infty dq\, f(q^2) \tag{4.10}$$

The integral can be evaluated, using the result (4.9) for $f(q^2)$, to give

$$\int_0^\infty dq\, f(q^2) = \pi\, b^3\sqrt{V/(12kTcb)} \tag{4.11}$$

The components of μ are related to the applied deformation by eq 4.4, so that finally for a uniaxial deformation

$$\langle \epsilon\{\mathbf{b}_j(t)\} V^*(\mu) \rangle_o = \frac{\nu_o}{N}K(\lambda^2 - \lambda^{-1}) \tag{4.12}$$

where K is an effective interaction parameter given by

$$K = \frac{1}{5\pi}\sqrt{\frac{12V}{cb^3kT}} \tag{4.13}$$

The full NMR interaction energy is the sum of the contribution from the cross-links (eq 3.3) and from the interactions (eq 4.12). It can be written as

$$\langle \epsilon(\mathbf{b}_j) \rangle_R = \frac{\nu_o}{N}\left\{\frac{2Z^2 - X^2 - Y^2}{Nb^2} + K(\lambda^2 - \lambda^{-1})\right\} \tag{4.14}$$

The implications of this result for the NMR results are discussed in the next section.

5. NMR Line Splitting

The relaxation of nuclear magnetization on the $\mathbf{b}_j$ bond in a network chain spanned by the vector $\mathbf{R}$ is given by

$$G(g;\mathbf{R}) = \cos\{\langle \epsilon\{\mathbf{b}_j) \rangle_{\mathbf{R}} t\} = \cos\left\{\frac{\nu_o}{N}\left[\left(2\lambda z_o^2 - \frac{x_o^2}{\lambda} - \frac{y_o^2}{\lambda}\right)t - K(\lambda^2 - \lambda^{-1})t\right\} \tag{5.1}$$

where x_o, y_o, and z_o are the scaled end to end vectors $x_o^2 = X_o^2/Nb^2$ etc. The averaging over the distribution of unperturbed end to end vectors $\{x_o, y_o, z_o\}$ is done using the Gaussian distribution function in eq 3.7 and was considered in section 3. For the noninteracting case, i.e., $K = 0$, the result was given in eq 3.8 as the Fourier transform $G_0(\omega;\mathbf{R})$. The full result (5.1) when Fourier transformed and averaged over the end to end vector $\mathbf{R}$ can be written in terms of this function as

$$G(\omega,\lambda) = \{G_0(\omega + \delta) + G_0(\omega - \delta)\}/2 \tag{5.2}$$

The term δ is responsible for the line splitting and is given by

$$\delta = (\lambda^2 - \lambda^{-1})\frac{\nu_o}{N}\sqrt{\frac{12V}{cb^3kT}} \tag{5.3}$$

The result is in agreement with the work of Sotta and Deloche[1] on strained poly(dimethylsiloxane) networks. The splitting is linear in $\lambda^2 - \lambda^{-1}$ and inversely proportional to N. However, they assumed that the direct segment–segment interactions had a nematic component parameterized by an interaction constant U. Their result for the term $\langle \epsilon\{\mathbf{b}_j\} \rangle_{\mathbf{R}}$ can be writtten as

$$\langle \epsilon\{\mathbf{b}_j\} \rangle_{\mathbf{R}} = \frac{3\nu_Q}{10N}\left\{\frac{2Z^2 - X^2 - Y^2}{Nb^2} + \frac{4}{9}\frac{U}{5 - U}(\lambda^2 - \lambda^{-1})\right\} \tag{5.4}$$

where ν_Q is the static quadrupolar interaction for a C–D bond. This has the same form as the present result (eq 4.13) if their term in U, coming from the nematic interactions, is identified with the second term of eq 4.13 coming from the anisotropically screened excluded-volume interactions.

The experimental results of Sotta and Deloche on the PDMS networks were fitted by $U = 0.5$, which implies that the splitting term $\delta = 0.049(\lambda^2 - \lambda^{-1})$. Using this value and the expression (3.8) for $G_0(\omega,\lambda)$, the full result (5.2) is shown in Figure 3 in terms of the scaled frequency variable $\omega N/\nu_0$ and for a range of deformations in both compression and extension.

6. Discussion

In a network, the constraint on the chain end to end vector $\mathbf{R}$ by the cross-link junction points prevents the individual bond vectors from completely reorientating. This results in a nonzero NMR interaction, which in turn leads directly to a splitting of the line shape. The magnitude of the splitting depends on the local orientation of $\mathbf{R}$, which in turn can be controlled by an applied deformation. However, the orientation of the deformed chain end to end vectors is related to those in the undeformed state, which are assumed to be isotropically distributed. When the line shape is averaged over the network, the superposition of all the individual splittings leads to a single broadened but unsplit line. The main conclusion from this is that a preferred direction, common to all the segments, must be established in the network. In the work of Sotta and Deloche this was achieved by

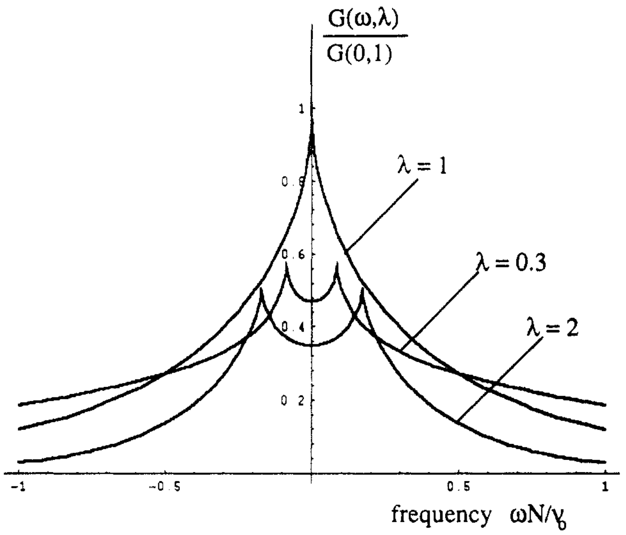

Figure 3. Effect of a uniaxial deformation λ on the NMR relaxation function given by eq 5.2, including the effect of screened interactions.

introducing nematic interactions between the segments similar to those found in liquid crystalline systems. In this paper an alternative mechanism was proposed, based on the screening properties of deformed network chains. Essentially such chains will behave like those in a melt and screen the isotropic short-range repulsive excluded-volume interactions with an induced attractive potential. However, unlike those in the melt, the network chains can be permanently deformed. The resulting screened potential, which is common to all the bonds, becomes anisotropic and dependent on the applied deformation. To order N^{-1} the anisotropy has a nematic form and leads to a line splitting, which for uniaxial deformations is linear in $\lambda^2 - \lambda^{-1}$ and inversely proportional to N.

Appendix 1. Evaluation of G(ω;λ)

For a uniaxial deformation, $G(\omega;\lambda)$ can be calculated from eqs 3.7, 3.5, and 3.3 in terms of the following integrals:

$$I_\pm(\omega;\lambda) = (2\pi N b^2/3)^{-3/2}\int\int\int \mathrm{d}X_0\,\mathrm{d}Y_0\,\mathrm{d}Z_0 \times \exp\left[-\frac{3}{2}\frac{X_0^2 + Y_0^2 + Z_0^2}{Nb^2}\right] \times \left[\delta\left\{\omega \pm \frac{\nu_0}{N}\left(\frac{2\lambda^2 Z_0^2 - \lambda^{-1}X_0^2 - \lambda^{-1}Y_0^2}{Nb^2}\right)\right\}\right]$$

as

$$G(\omega;\lambda) = \pi\{I_+(\omega;\lambda) + I_-(\omega;\lambda)\} \qquad \text{(A1.1)}$$

The integrals can be expressed in terms of scaled cylindrical coordinates

$$r^2 = \frac{X_0^2 + Y_0^2}{\lambda N b^2} \qquad z^2 = \frac{\lambda^2 Z_0^2}{Nb^2}$$

as

$$I_\pm(\omega;\lambda) = (2\pi/3)^{-3/2}\int_0^\infty \mathrm{d}r^2 \int_{-\infty}^{\infty}\mathrm{d}z\,\exp[-3(\lambda r^2 + \lambda^{-2}z^2)/2] \times \delta\left\{\omega \pm \frac{\nu_0}{N}(2z^2 - r^2)\right\} \qquad \text{(A1.2)}$$

The integral over r^2 is immediately done on account of the δ function. The two integrals I_+ and I_- must be treated separately. For I_+, $r^2 = N\omega/\nu_0 + 2z^2$, and since r^2 remains positive for all z, the remaining integral over z is unrestricted.

$$I_+(\omega;\lambda) = (2\pi/3)^{-3/2} N/\nu_0 \exp(-3N\omega\lambda/\nu_0)\int_{-\infty}^{\infty}\mathrm{d}z \times \exp(-3z^2(2\lambda + \lambda^{-2})/2) = (3/2\pi)N/\nu_0(2\lambda + \lambda^{-2})^{-1/2} \times \exp(-3N\omega\lambda/2\nu_0) \qquad \text{(A1.3)}$$

For I_-, $r^2 = -N\omega/\nu_0 + 2z^2$, and for r^2 to remain positive, the range of z is restricted to $|z| > z(\omega) = (N\omega/2\nu_0)^{1/2}$. Then

$$I_-(\omega;\lambda) = (2\pi/3)^{-3/2} N/\nu_0 \exp(3N\omega\lambda/2\nu_0) \times \left[2\int_{z(\omega)}^{\infty}\mathrm{d}z\,\exp(-3z^2(2\lambda + \lambda^{-2})/2)\right] = (3/2\pi)N/\nu_0(2\lambda + \lambda^{-2})^{-1/2}\exp(3N\omega\lambda/2\nu_0) \times \operatorname{erfc}\left(\sqrt{3N\omega(2\lambda + \lambda^{-2})/2\nu_0}\right) \qquad \text{(A1.4)}$$

erfc is the complementary error function. Substitution of I_+ and I_- into eq A1.1 leads to the result quoted in the paper.

Appendix 2. Calculation of the Term

$$\langle \epsilon\{\mathbf{b}_j(t)\}V^*(\mu)\rangle_0 = \frac{\nu_0}{\Omega b^2}\sum_{mnq} V_q^*(\mu)\langle(2b_{jz}^2 - b_{jx}^2 - b_{jy}^2)\exp(i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n))\rangle_0 \qquad \text{(A2.1)}$$

The statistical averages can all be obtained from the generating function

$$Z(\mathbf{h}) = \sum_{mn}\langle \exp(i\mathbf{q}\cdot\sum_{s=m}^{n}\mathbf{b}_s + \mathbf{h}\cdot\mathbf{b}_j)\rangle_0 \qquad \text{(A2.2)}$$

For example

$$\sum_{mn}^{n}\langle b_{jz}^2\exp(i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n))\rangle_0 = \frac{\mathrm{d}^2}{\mathrm{d}h_z^2}Z(\mathbf{h})|_{h=0}$$

The $\{\mathbf{b}_s\}$ are Gaussian random variables; i.e.

$$\langle \exp(\mathbf{b}_s\cdot\mathbf{A})\rangle = \exp(A^2\langle \mathbf{b}_s\rangle^2/2)$$

Hence, the generating function $Z(\mathbf{h})$ is given by

$$Z(\mathbf{h}) = \exp(h^2b^2/6)\sum_{mn}\exp\{-q^2b^2|m-n|/6 + i\mathbf{h}\cdot\mathbf{q}^2\Theta_{mn}(j)/3\} \qquad \text{(A2.3)}$$

where $\Theta_{mn}(j) = 1$ if j is in the range between m and n and zero otherwise. The sums can be converted into integrals

$$\sum_m \rightarrow \int_0^n \mathrm{d}m$$

to give

$$Z(\mathbf{h}) = 12\exp\left(\frac{h^2b^2/6}{q^2b^2}\right)\{N - F(j) - F(N-j)\} + 2\exp(i\mathbf{h}\cdot\mathbf{q}b^2/3)\,F(j)\,F(N-j) \qquad \text{(A2.4)}$$

where $F(j) = 6(1 - \exp(-jq^2b^2/6))/(q^2b^2) \simeq 6/(q^2b^2)$ for j not near the chain ends.

The averages in eq A2.1 can be generated using $Z(\mathbf{h})$ to give

$$\sum_{mn}\langle(2b_{jz}^2 - b_{jx}^2 - b_{jy}^2)\exp(i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n))\rangle_0 = \frac{8(2q_z^2 - q_x^2 - q_y^2)}{q^4} \qquad \text{(A2.5)}$$

The NMR interaction energy is given by

$$\langle \epsilon\{\mathbf{b}_j(t)\}V^*(\mu)\rangle_0 = \frac{8\nu_0}{b^2}\int \frac{\mathrm{d}^3q}{(2\pi)^3} V_q{}^*(\mu)\frac{1}{q^4}\{2q_z{}^2 - q_x{}^2 - q_y{}^2\}$$

where the sum over q has been replaced by an integral. When $V_q{}^*(\mu)$ is written in the form

$$V_q{}^*(\mu) = V_q{}^*(0) + (\mu\cdot\hat{q})^2 f(q^2)$$

and

$$\{2q_z{}^2 - q_x{}^2 - q_y{}^2\} = 2q^2 P_2(\cos\vartheta)$$

then only the term involving $\mu\cdot\hat{q}$ contributes to the integral. The angular terms can be integrated using the properties of spherical harmonics to give

$$\langle \epsilon\{\mathbf{b}_j(t)\}V^*(\mu)\rangle_0 = \frac{4\mu^2 P_2(\cos\chi)\nu_0}{5\pi^2 b^2}\int_0^\infty \mathrm{d}q\, f(q^2) \qquad \text{(A2.6)}$$

where χ is the angle μ makes to the z axis. In component form this is the result used in the paper.

References and Notes

(1) Sotta, P.; Deloche, B. *Macromolecules* **1990**, *23*, 1999.

(2) Sotta, P., et al. *Macromolecules* **1987**, *20*, 2769.

(3) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316.

(4) Deloche, B.; Samulski, E. T. *Macromolecules* **1981**, *14*, 575.

(5) Sotta, P.; Deloche, B.; Herz, J. *Polymer* **1988**, *29*, 1171.

(6) Brereton, M. G. *Macromolecules* **1991**, *24*, 6160.

(7) Brereton, M. G.; Vilgis, T. A. *J. Phys. 1 Fr.* **1992**, *2*, 581.

(8) Edwards, S. F.; Vilgis, T. A. *Rep. Prog. Phys.* **1988**, *51*, 243.

(9) Cohen-Addad, J. P. *J. Phys. 1 Fr.* **1982**, *43*, 1509.

(10) Cohen-Addad, J. P.; Dupeyre, R. *Polymer* **1983**, *24*, 400.

(11) Brereton, M. G.; Vilgis, T. A. *J. Phys. 1 Fr.*, submitted.

(12) Edwards, S. F. *J. Phys. A* **1975**, *8*, 1670.