Notes

Obtaining More from the Chemical Shift Anisotropy of Elastic Polymer Networks: A Simple Model To Account for the Distribution of Chain Lengths in a Network

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Information on details of the molecular structure of polymer networks, including parameters of irregularity such as the chain-length distribution, the number of dangling chains, and the deviation from uniformity in functionality of cross-links, is necessary for understanding the behavior of networks and developing an adequate theory.[1,2] It has been emphasized recently that there are relatively few experimental techniques for studying details of a polymer network structure.[3] Among these few, nuclear magnetic resonance methods play an increasingly important role. The general features and peculiarities of NMR in polymer networks are now well understood.[4-18] Less progress has been achieved in NMR elucidation of details of a polymer network structure, such as deviation from an ideal network. A number of obstacles preclude a rigorous treatment of this problem. One problem inherent in using ^{1}H NMR line shape for network studies is the difficulty in accounting for dipole interactions of spins close to each other in space but nonadjacent on a chain. Investigation of line shapes governed by one-spin Hamiltonians circumvents this problem, and ^{2}H NMR has proven to be very helpful.[14-18] However, since ^{2}H NMR is limited to networks labeled with deuterium, it is evident that approaches based on other one-spin Hamiltonians, such as chemical shift anisotropy (CSA), are desirable.[19,20] In this paper an attempt is made to use a simple model of a freely jointed chain to discuss the influence of irregularities of a network on a line shape governed by CSA.

When CSA dominates all other interactions, the resonance frequency ω is given by[21]

$$\omega = -\omega_0(2/3)^{1/2}\sigma_{20} \quad (1)$$

where ω is determined with respect to the reference frequency $\omega_0(1 - \sigma)$. Here $\omega_0 = \gamma\mathbf{B}$, where γ is the gyromagnetic ratio and $\mathbf{B}$ is the external magnetic field; σ is the isotropic shift seen in the solution, and σ_{20} is the irreducible component of the chemical shift tensor in the laboratory frame.

Several simplifying assumptions, analogous to those used in ref 18 for calculation of quadrupole splittings in a network, are made here in the evaluation of σ_{20}. The anisotropic axially symmetric segmental motion is assumed to be fast on the NMR time scale.[22] In this case averaging does not depend on the details of the motion and is usually modeled by averaging NMR parameters over different rotational angles or different conformational states.[23-25] The simple model of the freely jointed chain is known to be a good approximation for averaging over conformational states in theories of rubber elasticity[26,27] and of optical[28] and NMR properties[4-9,12,13,17,18] of elastic polymer networks. Another simplification frequently used in the affine theory of rubber elasticity and also in the analysis of NMR properties is the approximation of fixed cross-links;[4,9,13,17,18,26-28] the distance between neighboring cross-links in the undeformed state is assumed to be equal to (or near) the mean-square distance between the ends of the corresponding chain.[4,12,17,18,26,27] Using these simplifications and taking into account that very often molecular groups experience fast anisotropic intramolecular rotation in addition to the segmental motion, we arrive after the averaging (following procedures similar to those in ref 18) at

$$\omega = (S/2Z)(3\cos^2\beta'' - 1) \quad (2)$$

$$S = (3/80)\omega_0\delta(3\cos^2\beta_2 - 1)(3\cos^2\beta_1 - 1 + \eta\sin^2\beta_1\cos 2\alpha_1)$$

where Z is the length of the chain or the number of statistical segments between adjacent knots, α_1 and β_1 are the Euler angles which determine the direction of the intramolecular rotation axis in the principal coordinate system, β_2 is the angle that the intramolecular rotation axis makes with the direction of the statistical segment, β'' is the angle that the vector connecting adjacent knots makes with the direction of the external magnetic field, and the anisotropy parameter δ and asymmetry parameter η are usually represented[21] in terms of components σ_{pp} of the diagonalized shielding tensor: $\delta = \sigma_{zz} - \sigma$, $\eta = (\sigma_{yy} - \sigma_{zz})/(\sigma_{zz} + \sigma)$. The details of the analogous averaging procedure for the case of quadrupole splitting and a diagram showing the relationships among the angles and the elements of the model are presented in ref 18. A similar procedure can also be found in ref 17.

For a statistical network with random orientations of end-to-end vectors, the line shape $I(\omega,Z)$ is expressed as

$$I(\omega,Z) = (Z/3S)(1 + 2\omega Z/S)^{-1/2}, \quad -S/2Z < \omega < S/Z \quad (3)$$

In order to account for minor contributions to the line width, it is customary[21] to convolute the theoretical line shape with a Lorenzian or a Gaussian. Convolving eq 3 with a Lorenzian yields

$$J(\omega,Z) = \int_{-S/2Z}^{S/Z} I(\omega^*,Z)\,(\pi b(1 + (\omega - \omega^*)^2/b^2))^{-1}\,d\omega^* \quad (4)$$

where b is the Lorenzian width parameter. Only the situation when $b \ll SZ$ is of practical interest here, and this condition can often be achieved, especially in experiments with suppression of dipole interactions by a series of high power radio-frequency pulses.[21]

Equations 3 and 4 suggest that a line shape for an ideal network with uniform Z throughout the sample should not differ from a line shape for polycrystallites.[21] The resultant line shape shows an axial symmetry of the time-averaged CSA interactions whatever the initial CSA tensor; this is a consequence of the axial symmetry of the molecular motion. The line width $\Delta\omega = \omega_\parallel - \omega_\perp = 3S/2Z$ is proportional to the density of cross-linking (inversely

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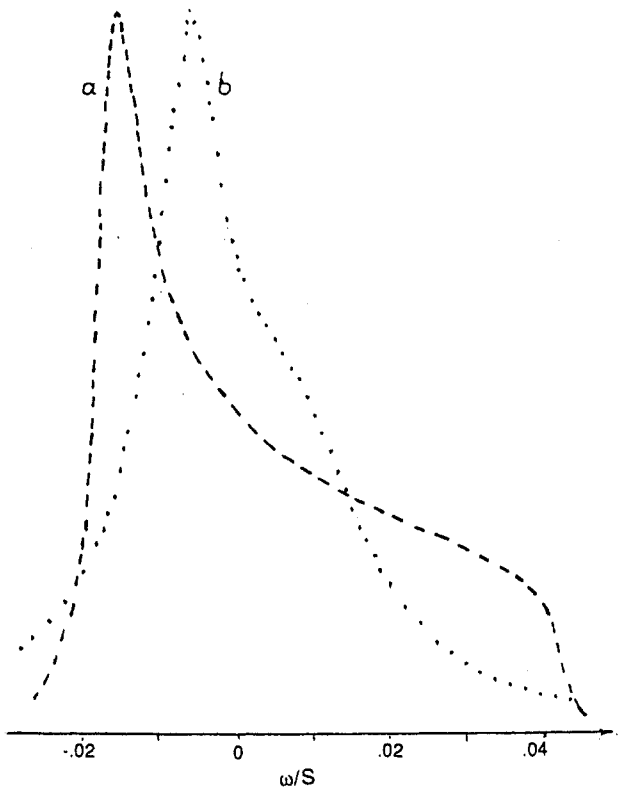

Figure 1. Calculated line shapes for the regular (a) network ($Z = 50$ and $b = S/10Z$ used for eq 4) and the irregular (b) network ($Z_0 = 50$, $\Delta Z = 50$, $b = S/10Z_0$, $Z_{min} = 1$, and $Z_{max} = 500$ used for eq 5).

proportional to the chain length Z). For a nonideal or irregular network, $Z \neq$ const and a distribution of chain lengths $\Phi(Z)$ should be considered. In this case eq 4 transforms to

$$G(\omega) = \int_{Z_{min}}^{Z_{max}} \Phi(Z)\, dZ \int_{-S/2Z}^{S/Z} I(\omega^*,Z)\, (\pi b(1 + (\omega - \omega^*)^2/b^2))^{-1}\, d\omega^* \quad (5)$$

It is evident that the nature of the distribution function $\Phi(Z)$ affects the line shape. For example, let us assume that $\Phi(Z)$ is given by the Gaussian $\Phi(Z) = A \exp(-(Z - Z_0)^2/(\Delta Z)^2)$, where Z_0 is the median chain length, ΔZ is the width of the distribution, and A is the normalization factor.

In Figure 1 the line calculated according to eq 5 with the Gaussian distribution is compared to an ideal network line shape (eq 4). For convenience, the lines of equal height are compared. The value of Z_0 is taken equal to the value of Z for an ideal network; both are equal to 50, which corresponds to a moderately cross-linked polymer. The dipole broadening b is 10 times less than the line width due to CSA; this proportion is often used for the purpose of convolution.[21] It is evident that the width of the distribution is the critical parameter actually determining the deviation of the line shape from the ideal one. The width generally depends on the way the network is synthesized and can be expected to differ significantly among different networks. There is no systematic experimental study of the distribution of network chain lengths in the literature. In the present work we use the information on the width of the distribution obtained in ref 18. This width was evaluated by fitting the experimental ^2H NMR lines of ref 15 for a deuterosubstituted network with the theoretical curves derived in ref 18. For this particular network, which was moderately cross-linked, the value of ΔZ is close to Z_0. Thus for line b in Figure 1 $\Delta Z = 50$ was used. Figure 1 shows that the ideal network line shape can differ significantly from the line for the network with the distribution of lengths. For an ideal network all chains have similar NMR behavior, and a polycrystal-type line shape with axial symmetry of the CSA tensor is expected. In irregular networks with a distribution of chain lengths and dangling chains the observed line is a superposition of signals from chains with different NMR behavior. Longer chains (or chains from areas with weaker cross-linking) contribute to the resultant signal with a narrower line, and this is reflected in the shape of line b in Figure 1. This line has a shape different from that characteristic of a polycrystallite with an axially symmetric CSA tensor and has an increased intensity at the central frequency compared to that of an ideal line a. Dangling chains, which are fixed to the network with only one end, should give the narrowest contribution since their motion is not restricted by inclusion in a network with both ends. Therefore, for dangling chains all tensorial interactions could in principle average out to zero. Line b in Figure 1 is calculated without consideration of dangling chains. Thus for a real network we should expect further deviation of a line shape from the ideal form, with an additional contribution of a narrow peak at the frequency $\omega_0(1 - \sigma)$.

The analysis of the proposed model shows that information about irregularities of a network is present in the CSA-dominated line shape. However, there are factors that could mimic the effect of a chain-length distribution besides the aforementioned possibility of the contribution of dangling chains. For example, the condition of fast motion could be satisfied for the segments which are far from the cross-links and not satisfied for those which are close to the cross-links. The presence of entanglements is another factor which is ignored here as well as in the affine and phantom theories of elasticity,[27,28] although entanglements are known to play an important role both in elastic and in NMR properties. As mentioned above, the fixed-cross-link approximation is often used in theoretical descriptions of polymer networks. This approximation reflects the fact that cross-links impose permanent restrictions on the chain motion, in principle preventing isotropic averaging. The last statement is strongly supported by NMR studies of polymer networks.[4-9,12-18] The assumption of restricted motion of the cross-links around their equilibrium positions is also consistent with the experimental fact that the tensorial interactions do not average to zero. It can be expected that the contribution of the restricted motion of the cross-links could further narrow the line, making adequate analysis more difficult.

In order to confirm the applicability of the suggested model for obtaining information on the structure of a network, it is necessary to study CSA-determined line shapes in networks which have already been independently characterized with respect to the chain-length distribution and other deviations from an ideal structure. Such experimental data seem to be unavailable in the literature at this time.

A conclusion that can be drawn on the basis of this simple model is that an irregular network line shape governed by CSA can differ from the ideal network line shape; the line shape for an irregular network acquires additional intensity at the central frequency compared to the ideal network, which has the line shape typical for a polycrystallite with axial symmetry of the CSA tensor. Since the line shape governed by CSA can reflect the character of the chain-length distribution function, its potential for being used in the elucidation of details of the structure of an elastic polymer network needs further investigation.

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