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Short-Range Nematic-like Orientational Order in Strained Elastomers: A Deuterium Magnetic Resonance Study[†]

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ABSTRACT: The orientational order generated in uniaxially strained elastomers is probed with deuterium NMR. Perdeuterated swelling agents exhibit quadrupolar splittings which have an explicit dependence on the extension ratio, degree of swelling, and temperature. A phenomenological description based on a lattice model of the deformed, swollen network which includes short-range nematic-like interactions successfully accounts for the observations. The implications that these findings have for the opticoelastic behavior of swollen networks are emphasized.

Introduction

The elastic and opticoelastic characteristics of rubbers have been studied extensively.[1-3] The classical kinetic or gaslike theory of rubber elasticity is based on ideal, volumeless, Gaussian chains suspended between a constellation of network junctions which deforms affinely. At low deformations there appears to be qualitative agreement between theory and experiment. However, closer inspection reveals inconsistencies: stress–strain data behave classically only in highly swollen networks;[3] stress–optical data are sensitive to ill-defined characteristics of the swelling agent.[4-6] This latter difficulty impedes a confident comparison of stress–optical behavior of a given elastomer with the configurational properties of the constituent chains in the context of the rotational isomeric state scheme.[5,7]

In general, the deviations from the classical theory have been ascribed to short-range orientational correlations between chain segments in the deformed network (segment–solvent correlations may persist in swollen networks). Modification of the theory to account for such correlations started with DiMarzio's generalization of the classical lattice theory to include the volume of the chain segments and the consequent packing entropy;[8] these ideas have been extended more recently.[9,10] Addressing this problem from the viewpoint of liquid crystal physics, de Gennes considered the effect of a nematic-like interaction (uniaxial orientational field) on network chains composed of nematogenic segments;[11] explicit results relevant to rubber elasticity were subsequently reported.[12] Herein we interrelate these various theoretical approaches via a phenomenological description of new experimental data resulting from a unique probe for short-range orientational order, deuterium nuclear magnetic resonance (^{2}H NMR).

^{2}H NMR has been extensively used to probe local orientational correlations in liquid crystals.[13] Here we use it to probe the local environment within swollen rubber networks under simple uniaxial tension. We focus on the orientational order parameter of labeled swelling agents; it exhibits a distinctive dependence on the network extension ratio, volume fraction, and temperature. Inclusion of a nematic-like short-range coupling into the expression for the free energy in a lattice model of the deformed network yields an explicit relationship among the network variables which is in good agreement with the experimental results. An extension of this description to opticoelastic behavior can readily account for the observed dependence of the stress–optical coefficient on the degree of swelling and explicit characteristics of the swelling agent. Moreover, this phenomenological description rigorously corroborates earlier empirical conclusions suggesting that the intrinsic configurational properties of isolated chains can only be extracted from the stress–optical coefficients measured in highly swollen elastomers employing optically isotropic swelling agents.

Background

A. Opticoelasticity. The stress–optical behavior of deformed elastic networks is usually interpreted in terms of the kinetic theory of Kuhn and Grün.[14] For uniaxial tension this theory leads to a relation between the true stress t (referred to the strained cross section) and the extension ratio λ

$$t = N_c kT(R^2/R_0^2)(\lambda^2 - \lambda^{-1}) \tag{1}$$

N_c is the number of active network chains per unit volume, R^2 is the mean-square end-to-end distance of chains in the unstressed network, and R_0^2 is the corresponding value for chains free from perturbations imparted by the network or by long-range interactions.[15] The stress-induced birefringence of the network, Δn, is related to the mean refractive index of the network, $\bar{n}$, and the uniaxial polarizability anisotropy of the *ideal* freely jointed chain segment, $\Delta\alpha^*$, by

$$\Delta n = (2\pi/45)N_c\Delta\alpha^*[(\bar{n}^2 + 2)^2/\bar{n}](R^2/R_0^2)(\lambda^2 - \lambda^{-1}) \tag{2}$$

The ratio $\Delta n/t$ defines the stress–optical coefficient, C

$$C = (2\pi/45kT)[(\bar{n}^2 + 2)^2/\bar{n}]\Delta\alpha^* \tag{3}$$

which according to the classical theory is independent of N_c and λ. Experiment generally supports this prediction but the observed strong dependence of C on the degree of swelling of the network[1-7,16,17] is not accounted for, as both t and Δn are affected in the same way by dilution of the network chains.

On close examination C does not follow the simple T dependence of eq 3. The residual temperature dependence, usually expressed as d ln $\Delta\alpha^*/\mathrm{d}T$, is believed to be accounted for by more elaborate molecular theories of C using the rotational isomeric state scheme.[18-24] In practice, the T dependence of $\Delta\alpha^*$ is found to be consonant with the T dependence of the statistical weights of the rotational isomeric states of a specific elastomer only for highly swollen networks and a judicious choice of swelling agents.[5,7]

B. Deuterium Nuclear Magnetic Resonance. Molecular motion in macroscopically anisotropic fluid media does not average some magneto- and electrostatic interactions to zero. The dipole–dipole interaction among magnetic nuclei and the electric field gradient (efg) are two tensor quantities which, if incompletely averaged, can markedly perturb the conventional NMR spectroscopy of the affected molecules.[25] Liquid crystals (or probe mole-

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cules solubilized in liquid crystalline fluids) provide striking examples of this phenomenon.[13] The proton NMR spectrum of mesogens (or of probes with several inequivalent hydrogens) is distorted to a broad, featureless spectrum spanning tens of kilohertz because of the strong proton–proton dipolar interactions. Such distortions are negligible for most quadrupolar nuclei as their magnetic moments are relatively small. For quadrupolar nuclei with spin = 1 such as the deuteron, the quadrupole moment's interaction with the partially averaged efg lifts the degeneracy of the two transitions associated with the three Zeeman levels. Hence the ^{2}H NMR spectra of deuterium-labeled mesogens (or labeled probes) become a superposition of discrete doublets, $\Delta\nu_i$, one for each of the i inequivalent deuterons in the molecule.

The formalism that has developed to relate the dipolar and quadrupolar interactions in oriented, uniaxial liquid crystals to the average orientation of the relevant molecule employs a symmetric, traceless order tensor, **S**.[26] The elements of **S** are time-averaged values of products of the direction cosines l_α relating the axes of a molecular Cartesian xyz frame to the constraint or symmetry axis of the medium. In uniaxial nematic liquid crystals wherein the constraint direction is defined by the apolar director d, the tensor elements are

$$S_{\alpha\beta} = \langle {}^1\!/_2(3l_\alpha l_\beta - \delta_{\alpha\beta})\rangle \qquad (4)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta (α, β = x, y, z). The number of independent elements $S_{\alpha\beta}$ depends on the symmetry of the molecule under consideration. For molecules with C_3 or higher symmetry the number of elements is reduced to one, S_{zz}, the principal element (the z axis is the molecular symmetry axis).

In the case of a deuterated probe molecule with high symmetry, the quadrupolar splittings $\Delta\nu_i$ are directly related to the principal element S_{zz} by

$$\Delta\nu_i = {}^3\!/_2(e^2qQ/h)_i P_2(\cos\Omega) P_2(\cos\theta_i) S_{zz} \qquad (5)$$

where $(e^2qQ/h)_i$ is the static quadrupolar coupling constant of the ith deuteron (we make the usual assumption of an axially symmetric efg tensor with its principal value along the ith C–D bond). The P_2 terms are second Legendre polynomials; Ω is the angle between the constraint d and the spectrometer magnetic field $\vec{H}$, and θ_i is the angle between the ith C–D bond and the probe molecule's z axis.[26]

S_{zz} is the orientational order parameter of the probe symmetry axis relative to the constraint d. For a perfectly oriented probe the corresponding values for S_{zz} are +1.0 ($z \| d$) or −0.5 ($z \perp d$); if the probe samples all orientations of z relative to d with equal probability on the NMR time scale ($\sim 10^{-6}$ s), then $S_{zz} = \Delta\nu = 0$. The value of S_{zz} extracted from the NMR experiment on probe molecules is, as is characteristic of all probe techniques, an indirect measure of the orientational order of the medium itself, S

$$S_{zz} = gS \qquad (6)$$

g is a proportionality factor which depends on the nature of the medium and physicochemical properties of the probe such as probe shape anisotropy, specific interactions, e.g., H bonding and electrostatic interactions. However, a large body of data on liquid crystals suggests that g, while characteristic of a given probe and medium, is not intrinsically very temperature dependent. Changes in $\Delta\nu(S_{zz})$ with external constraints, therefore, primarily reflect changes in the orientational behavior of the medium.

NMR has been used for some time to monitor probe orientation in fibrous proteins.[27] There are examples of the application of this technique to synthetic fibers as well.[28] And there are observations of dipolar interactions in the proton NMR spectra (dipolar splittings[29] and line broadening[30]) of swelling agents in strained elastomers. The ^{2}H NMR technique is, however, a more powerful technique for probing these latter systems. The current resolution available for observing $\Delta\nu$ ($\sim$1 Hz) in conjunction with the inherently large value of the C–D quadrupolar coupling constants e^2qQ/h ($\sim$200 kHz) enables one to measure (eq 5) probe orientational order differing from the isotropic state by as little as a few parts in 10^5.

Experimental Section

A. Sample. A commercial polyisoprene predominantly cis (Natsyn 2200; Goodyear Corp.) with a sulfur cure (nominal size 1.4 mm × 0.9 mm × 10 mm) was used in our study (Plymouth Rubber Co., Inc.; Revere size 16). The modulus $G \simeq 6.65 \times 10^4$ kg/m^2 and the average molecular weight between cross-links $M_c \simeq 3500$ (the number of monomer segments/network chain is roughly 50) as determined from stress–strain data at low elongation; swelling measurements indicate a somewhat lower range for M_c, 2300–2900. Prior to using, the sample was extracted with benzene for 12 h.

Preweighed samples of dry elastomer were exposed to the vapor/liquid of the swelling agents (commercial perdeuterated solvents were employed) and the volume fraction of polymer, ϕ, was determined by weighing the samples before and after the NMR experiment (additivity of polymer (ρ = 0.92 g/cm^3) and solvent volumes was assumed). As the measurements were carried out in a capped NMR tube, the uncertainty in ϕ was approximately 5%. We used an optical determination of the extension ratio, $\lambda = L/L_0$, where L and L_0 are the strained and unstrained lengths of the swollen elastomer, respectively; L was determined to within ±0.2 mm.

B. NMR. A commercial Fourier transform NMR spectrometer (Bruker WH-90) with deuterium observation at 13.82 MHz and an external deuterium lock was used. A conventional 5-mm NMR tube was modified with a Teflon bottom to hold the elastomer, and a glass insert through the cap enabled simple uniaxial extension of the sample. The stress constraint d is coincident with the tube axis and at right angles to the spectrometer magnetic field (Ω = 90° in eq 5). With the less than optimum filling factor and the decrease in effective sample size with increasing λ, signal averaging was necessary but not prohibitive.

Results

Figure 1 shows the transformation in the ^{2}H NMR spectrum of hexadeuteriobenzene (C_6D_6) in the rubber network (ϕ = 0.5) from a single line (λ = 1, isotropic medium) to a quadrupolar doublet as the uniaxial stress increases. The finite values for $\Delta\nu$ are indicative of anisotropic reorientational diffusion for C_6D_6 constrained by the uniaxial field generated by the deformed network chains. The phenomenon is quite general; similar results were observed in swollen poly(dimethylsiloxane) networks. The observed line width, $\sim$35 Hz, is probably determined by bulk magnetic inhomogeneity effects resulting from the sample holder and the noncylindrical sample shape (the samples were not spinning).

Figure 2 demonstrates that nearly spherical swelling agents ($CDCl_3$) as well as completely flexible swelling agents (n-heptane-d_{16}) exhibit anisotropic reorientational diffusion in the deformed network. For those solvents with more than one type of deuteron, multiple quadrupolar doublets are present in the spectrum. The $\Delta\nu$ can be assigned with a knowledge of the chemical shifts and intensities of the various types of deuterons. For p-xylene-d_{10}, there are two overlapping doublets; the upfield intense doublet is due to the CD_3 groups and the low-field doublet is from the ring. In the network swollen with n-heptane-d_{16} the central doublet corresponds to the ter-

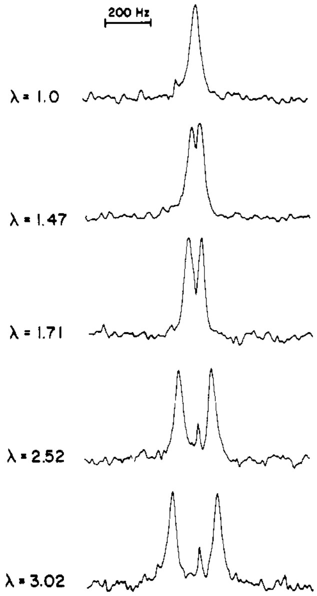

Figure 1. Evolution of quadrupolar splittings in the deuterium NMR spectra of the swelling solvent C_6D_6 for a rubber network (polymer volume fraction $\phi \simeq 0.5$) as a sample is uniaxially elongated. The extension ratio λ is relative to the swollen, unstrained state. The small central resonance apparent at large λ is attributed to isotropic C_6D_6 in the vapor phase.

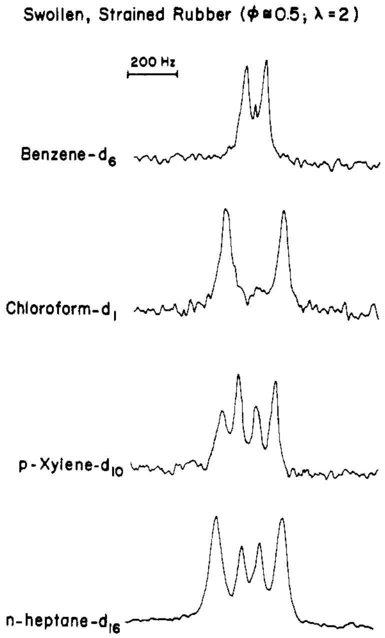

Figure 2. Deuterium NMR spectra of C_6D_6, $CDCl_3$, p-xylene-d_{10}, and n-heptane-d_{16} used as swelling agents in a strained rubber network ($\lambda = 2$; $\phi \simeq 0.5$). The latter two solvents have chemically inequivalent deuterons and exhibit more than one quadrupolar doublet. Additionally, the lower symmetry of the latter solvents requires more than one order parameter, $S_{\alpha\beta}$, to specify the solvent orientation. As the observed $\Delta\nu$ will be determined by a linear combination of the $S_{\alpha\beta}$, a comparison of solvent orientational order among the four swelling agents by simple inspection of the $\Delta\nu$ is precluded.

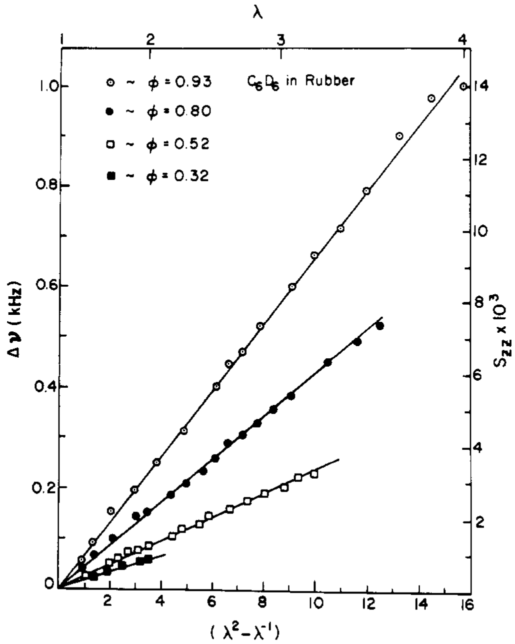

Figure 3. Quadrupolar splitting $\Delta\nu$ (left ordinate) and calculated order parameter S_{zz} (right ordinate) of C_6D_6 in the rubber network vs. $\lambda^2 - \lambda^{-1}$ for various degrees of swelling (ϕ). The observed $\Delta\nu$ are completely reversible with the extension ratio λ.

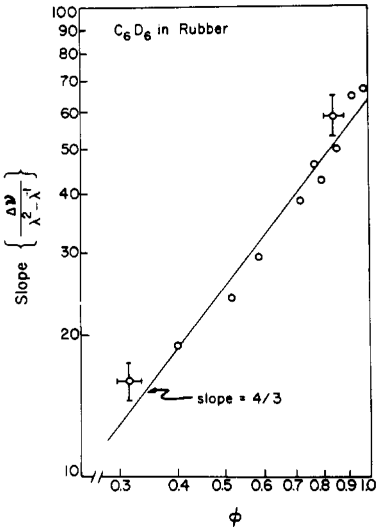

Figure 4. Slopes of $\Delta\nu$ vs. $\lambda^2 - \lambda^{-1}$ data of the type shown in Figure 3 plotted against polymer volume fraction ϕ on a log-log scale. Within the experimental uncertainties (indicated) the data exhibit a ϕ^m dependence, where $m = {}^4/_3$ (straight line).

minal CD_3 groups; the individual methylene doublets are superposed within the larger outer doublet and can be resolved only at high λ.

Figure 3 illustrates that $\Delta\nu$, for networks swollen with C_6D_6 to different volume fractions of elastomer, is a linear function of $\lambda^2 - \lambda^{-1}$. The variation of $\Delta\nu$ with λ is completely reversible with the strain; the range of λ for highly swollen networks is limited by the breaking tensile strength of the sample. The right-hand ordinate in Figure 3 shows the orientational order parameter of the benzene C_6 axis, S_{zz}, calculated with eq 5 with $\Omega = \phi = 90°$ and $e^2qQ/h = 190$ kHz. The values of this order parameter are similar in magnitude to those found for solvent molecules in lyotropic polymeric liquid crystals;[31] S_{zz} is about 2 orders of magnitude smaller in the swollen network than that observed for the C_6D_6 probe in thermotropic liquid crystals.[32]

Figure 4 is a log-log plot of the slopes $\Delta\nu/(\lambda^2 - \lambda^{-1})$, derived from data of the type shown in Figure 3, vs. volume fraction of network chains. The plot shows that the ϕ dependence of $\Delta\nu$ is of the form ϕ^m, where within the experimental uncertainties, $m = {}^4/_3$.

Discussion

The solvent acquires nonzero average orientational order as it diffuses[33] through the deformed fluid elastomer. It appears in the ^{2}H NMR spectrum of labeled swelling agents in the form of discrete quadrupolar splittings. This general behavior is evidence for a nematic-like orientational field in the *deformed* network that has its origins in the short-range interactions between partially aligned chain segments. Nematic-like interactions will in turn enhance segment orientational order above that anticipated by the affine deformation of isolated chains. The enhanced segment orientational order and concomitant reduction in the stress in the presence of the nematic interaction have been examined theoretically before;[8-12] a recent complementary treatment of this subject considered an elastomeric network swollen with an actual nematogenic solvent.[34] In the following section we cache this problem in the framework of a lattice model of the swollen network which includes the effects of the nematic-like field probed by the labeled swelling agent; explicit relationships among the equilibrium degree of nematic-like order, S, the degree of swelling of the network, ϕ, and the network deformation, λ, are derived.

A. Lattice Model. The presence of nematic-like interactions among the chain segments in a lattice model of a swollen regular network under uniaxial tension will modify the usual expression for $\mathcal{F}$, the free energy per site,[35] in the following way:

$$\mathcal{F}/kT = (1-\phi)\ln(1-\phi) - \frac{fa^3}{kT}(\lambda - 1) + \frac{\phi}{2}AS^2 + (1-\phi)\frac{AS^2}{2} + \phi(1-\phi)\left(\chi_0 + \frac{\chi_1}{2}S^2\right) + \frac{1}{2}\frac{\phi R^2}{NR_0{}^2}\left[\lambda^2\left(1 - ES + \frac{1}{2}FS^2\right) + \frac{2}{\lambda}\left(1 + \frac{ES}{2} - \frac{1}{4}FS^2\right)\right] \tag{7}$$

The first two terms correspond to the translational entropy of the solvent and the energy associated with the nominal stress f induced in the network by the strain λ (low-deformational limit, $\lambda < 2$); ϕ is the fraction of lattice sites (each with volume a^3) occupied by chain segments. The orientational order associated with the mean field is characterized by the orientational order parameter S; the remaining terms involve the effect of this nematic-like mean field.

First, there are two terms quadratic in S which represent the coupling of the segments and the coupling of the solvent with the nematic field with a coupling constant A assumed to be identical for both species. For systems which spontaneously form an ordered phase with no external constraints imposed (e.g., liquid crystals), A has the form $a(T - T^*)$, where T^* corresponds to the temperature limit of metastability of the isotropic phase.[36] As conventional chain segments and solvents have little propensity for spontaneous ordering, $T^* < T$ and, therefore, $A > 0$. The modification of segment–solvent interactions (χ_0) due to orientation correlations is expected to be negligible ($\chi_1 \ll 1$) for conventional segment–solvent species and this contribution to $\mathcal{F}$ will be ignored in subsequent expressions. The final term in eq 7 represents the Gaussian entropic elasticity (constant volume and affine deformation are assumed) modified by the presence of the nematic-like interactions. In the coefficient of this term, N is the number of chain segments beween cross-links, R_0 corresponds to the unperturbed dimensions of the chain, and R represents the dimensions in the swollen, undeformed network; R is related to ϕ by the packing condition $\phi R^3/a^3 = N$. The operationally ill-defined coefficient (Q in notation of ref 35) dependent on network functionality is set to unity. The entropic term is decomposed into interactions along the constraint direction d and those normal to d. In the former, to first order the coupling of the segments with S for a given λ decreases the elastic energy by an amount proportional to $-ES\lambda^2$ (the negative sign for this term has been discussed before[11]); $F \ll E$.

The equilibrium value of S, the nematic-like order generated in the deformed network, may be obtained by minimizing the free energy at fixed λ and ϕ. $\partial\mathcal{F}/\partial S = 0$ yields in the limit $F/N \ll A$

$$S \simeq \frac{1}{N}\frac{\phi E}{2A}\frac{R^2}{R_0{}^2}(\lambda^2 - \lambda^{-1})\left[1 - \frac{1}{N}\frac{\phi F}{2A}\frac{R^2}{R_0{}^2}(\lambda^2 - \lambda^{-1})\right] \tag{8}$$

This expression can be further simplified in the case of low deformations ($\lambda^2/N \ll 1$) to give

$$S \simeq \frac{1}{N}\frac{\phi E}{2A}\frac{R^2}{R_0{}^2}(\lambda^2 - \lambda^{-1}) \simeq \frac{\phi E}{A}S^*_{\text{seg}} \tag{9}$$

where S^*_{seg} is readily identified as the *ideal* segment order parameter deduced from kinetic theories of rubber elasticity.[37] The λ dependence of the quadrupolar splittings of the solvent (Figure 3) is in excellent agreement with the predictions of eq 9. The magnitude of the factor $\phi E/A$ can be estimated from $\Delta\nu$ (eq 5 and 6) with values for g and N; e.g., for $\phi = g = 1$ and $N = 100$ we obtain $\phi E/A \simeq 1$.

The presence of the nematic-like interaction results in an enhancement of the segment orientational order by the amount $(\phi E/A)S^*_{\text{seg}}$. When this enhancement is combined with the orientation caused by the affine deformation of the *ideal* chain, S^*_{seg}, the total segment orientational order is given by

$$S_{\text{seg}} = S^*_{\text{seg}}(1 + \phi E/A) \tag{10}$$

Identical expressions for S_{seg} were derived by Jarry and Monnerie[12] with a statistical calculation of a three-chain model of the network and by Tanaka and Allen[10] from the consideration of packing entropy using a lattice model.

B. Network Swelling. The Tanaka and Allen treatment of this problem provides a starting point for inferences about the ϕ dependence of the coupling coefficients E and A. The enhancement factor $\phi E/A$ is identified with their factor G (eq 20 in ref 10)

$$G = \phi E/A = [4e(3 - \phi)/9\phi - 1]^{-1} \tag{11}$$

The ϕ dependence of G was derived by these workers for two models: a random lattice walk and a restricted lattice walk for which the parameter e in eq 11 is $^9/_4$ and $^{27}/_8$, respectively. The computed ϕ dependence of G (see Figure 1 of ref 10) can be contrasted with experimental data of the type shown in Figure 3. For fixed λ, we anticipate that $\Delta\nu/(\lambda^2 - \lambda^{-1})\phi^{-2/3} \propto G$ (see eq 5, 6, and 9; note: $R^2 \propto \phi^{-2/3}$).

In Figure 5 we show $\Delta\nu/(\lambda^2 - \lambda^{-1})\phi^{-2/3}$ renormalized to 1.0 and 0.5, respectively, for the dry network ($\phi = 1$), derived from the slopes of $\Delta\nu$ vs. $\lambda^2 - \lambda^{-1}$ plots (Figure 3). The general agreement between experiment and the computed ϕ dependence[10] (solid lines) is quite good; the experimental uncertainty does not warrant a distinction between the two network models. Also shown in Figure 5 is a hypothetical ϕ^2 dependence of the short-range enhancement factor; namely, $\phi E/A \propto \phi^2$ (dotted line). This ϕ^2 dependence is close to the computed behavior of G and the experimental observations. Moreover, if we combine this ϕ^2 dependence in eq 9 with the ϕ dependence of the chain dimension, $R^2 \propto \phi^{-2/3}$, we find $\Delta\nu \propto gS \propto \phi^{4/3}$. The quadrupolar splittings of the solvent do, in fact, demon-

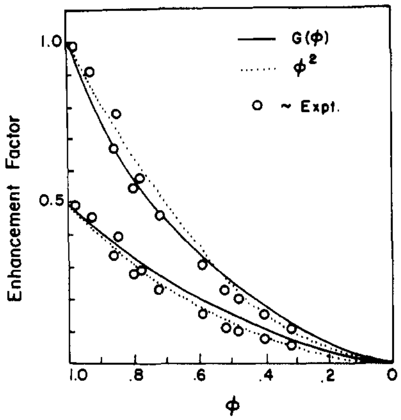

Figure 5. Computed ϕ dependence of G (eq 11) derived by Tanaka and Allen[10] (solid lines) and a ϕ^2 dependence (dotted lines); the random lattice walk and restricted lattice walk models of the swollen network correspond to intercepts of 1.0 and 0.5, respectively. The experimental data for the exhancement factor $\phi E/A$ are derived from Figure 3 by dividing by $\phi^{-2/3}$ (see text) and then renormalizing to 1.0 and 0.5 for $\phi = 1$.

strate the $\phi^{4/3}$ behavior (Figure 4). Hence, it appears that the changes in the nematic-like interactions within the deformed network on dilution are satisfactorily accounted for and reflected in the diluent anisotropic rotational diffusion sampled by the ^{2}H NMR experiment.

C. Stress-Optical Behavior. The description of a strained, swollen network with nematic-like interactions can be readily extended to opticoelastic phenomena. Letting the polarizability of the swollen network along the constraint director d, $P_{\parallel}$, and that normal to d, $P_{\perp}$, be additive functions of the appropriately weighted contribution from the partially oriented chain segments and solvent molecules, we find

$$P_{\parallel} - P_{\perp} = \frac{\phi}{a^3}\Delta\alpha^* S_{\text{seg}} + \frac{1-\phi}{a^3}\Delta\alpha' gS \qquad (12)$$

In eq 12 it is implicitly assumed that the segment and solvent polarizability anisotropies, $\Delta\alpha^*$ and $\Delta\alpha'$, respectively, are derived from ideal uniaxially symmetric entities; S_{seg} and gS (see eq 6) specify the average orientation of the respective symmetry axes relative to d. The birefringence of the network, Δn, follows from eq 12 if we utilize the Lorentz-Lorenz relation and the standard approximation[38] relating the differences in principal segment (solvent) refractive indices to a mean refractive index n_0:

$$\Delta n = \frac{4\pi}{18}\frac{(n_0^2+2)^2}{n_0} N_c \Delta\alpha \frac{R^2}{R_0^2}(\lambda^2 - \lambda^{-1}) \qquad (13)$$

N_c, the number of chains per unit volume, is given by $N_c^{-1} = \phi^{-1}Na^3$; for algebraic simplicity, we assume the mean refractive indices of a segment and a solvent molecule are identical in eq 13. Using the equilibrium order parameters derived from the lattice model in eq 12, we find that the polarizability anisotropy in eq 13, unlike that in the classical kinetic theory (eq 2), consists of three components as in eq 14: the ideal segment anisotropy, an enhancement

$$\Delta\alpha = \Delta\alpha^*\left[1 + \frac{\phi E}{A} + (1-\phi)\frac{\Delta\alpha'}{\Delta\alpha^*}g\frac{E}{A}\right] \qquad (14)$$

due to short-range interactions of the segments with the nematic field, and a component from the partially oriented optically anisotropic swelling agent.

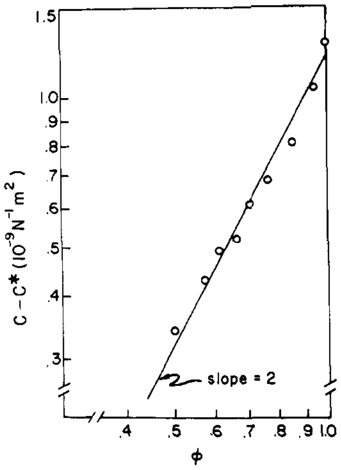

Figure 6. Stress-optical coefficient data of Gebhard et al.[17] for *trans*-1,5-polypentamer swollen with CCl_4 in the form of $C - C^*$ plotted vs. volume fraction of polymer ϕ on a log-log scale; the intrinsic value $C^* \simeq 2.0$ is obtained from the limiting value of C as $\phi \rightarrow 0$. The solid line corresponds to a ϕ^2 dependence for the quantity $C - C^*$.

In order to obtain the stress-optical coefficient from eq 13, we find the equilibrium true stress t in the lattice model by setting $\lambda(\partial\mathcal{F}/\partial\lambda) = 0$

$$t = N_c kT\frac{R^2}{R_0^2}\left[(\lambda^2 - \lambda^{-1}) - \frac{1}{4}\frac{\phi}{N}\frac{E^2}{A}\frac{R^2}{R_0^2}\left(2\lambda^4 - \lambda - \frac{1}{\lambda^2}\right)\right] \qquad (15)$$

The negative correction term to the classical stress (see eq 1) arising from the nematic interaction may be neglected at low deformations ($\lambda^2/N \ll 1$); this term was originally investigated in the context of the Mooney-Rivlin equation.[9,10,12] Using the first term in eq 15 and eq 13 and 14, we find for the stress-optical coefficient

$$C = C^*\left[1 + \frac{\phi E}{A} + (1-\phi)\frac{\Delta\alpha'}{\Delta\alpha^*}g\frac{E}{A}\right] \qquad (16)$$

where $C^* = (4\pi/18)[(n_0^2 + 2)^2/kTn_0]\Delta\alpha^*$ is, within a multiplicative constant, identical with that derived from the classical theory (eq 3).

It is clear from the limiting cases of eq 16 that intrinsic properties of isolated chains ($\Delta\alpha^*$) are not simply derived from the quotient $\Delta n/t$. For dry networks ($\phi = 1$) the nematic interaction among segments in the form of the ratio of the coupling coefficients, E/A, contributes to C. Hence chains with differing monomer primary structures will exhibit different stress-optical coefficients via differences in $\Delta\alpha^*$ *and* the strength of their respective couplings with the nematic-like field. The latter effect does not preclude considerable differences in C for dry networks having only small differences in $\Delta\alpha^*$ (originating in stereochemical differences in the chain primary structure), e.g., the *cis*- and *trans*-1,4-butadienes.[6]

It is also apparent from eq 16 that when the network chains are diluted ($\phi \neq 1$) by an optically isotropic solvent ($\Delta\alpha' = 0$), the short-range interactions among the segments are screened. Further, utilizing the approximate ϕ^2 dependence found in section B for the enhancement factor $\phi E/A$, we anticipate that $C - C^* \propto \phi E/A \propto \phi^2$. In Figure 6 we demonstrate that $C - C^*$ does, in fact, exhibit the anticipated ϕ^2 dependence, using recent measurements of C in samples of 1,5-polypentamer swollen with CCl_4.[17] In principle, C^*, and thereby the intrinsic anisotropy of the segment polarizability $\Delta\alpha^*$, can be obtained from mea-

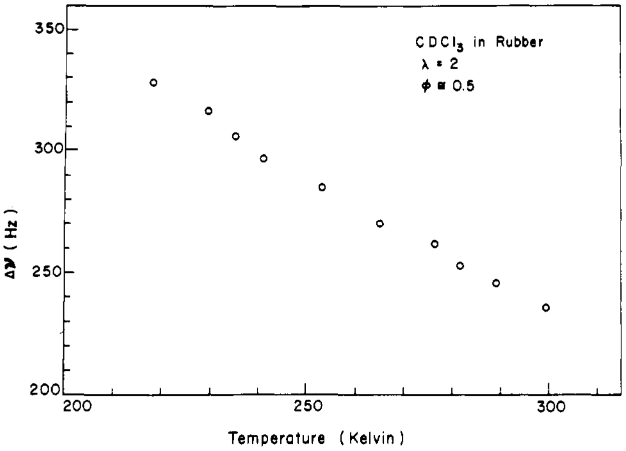

Figure 7. Quadrupolar splitting of the swelling agent $CDCl_3$ in a strained rubber network ($\lambda = 2$, $\phi \simeq 0.5$) vs. temperature.

surements of C in the limit $\phi \rightarrow 0$ when the solvent anisotropy $\Delta\alpha' = 0$.

When the network is swollen with an optically anisotropic solvent ($\Delta\alpha' \neq 0$), there is an additional contribution to C, the third term in eq 16. Moreover, as there is no a priori method for predicting the sign (or magnitude[39]) of g, the proportionality factor relating the average solvent orientational order to that of the nematic field, this contribution could increase or decrease observed values of C in swollen networks relative to the value of C in the dry network. A case in point is *cis*-polyisoprene, wherein reported values of C (m^2/kg) are 1.90, 1.55, and 2.15 for the unswollen elastomer, that swollen with benzene, and that swollen with *p*-xylene, respectively.[4] (Note that since the symmetry of *p*-xylene is less than C_3, the uniaxial description of network polarizability (eq 12) is not applicable.[40])

Lastly, we consider the effect of temperature on the nematic-like contributions to C. In Figure 7 we show that the quadrupolar splitting of a network swollen with $CDCl_3$ is dependent on temperature. Admittedly, the temperature dependence of $\Delta\nu$ may be due in part to changes in probe–medium interactions that affect g (eq 6 and 9). It is probably dominated, however, by changes in the nematic interactions with temperature (S^*_{seg} is independent of temperature). If we use the slope of the $\Delta\nu$ vs. T data in Figure 7, we can estimate the magnitude of the temperature dependence of $\mathrm{d}\ln C/\mathrm{d}T$ due to those terms involving the nematic coupling. We find, using eq 5, 6, and 9 that for $\phi = 0.5$ and $g \approx 1$, $\mathrm{d}\ln (E/A)/\mathrm{d}T \approx N \times 10^{-5}$. Hence for moderate swelling and reasonable values for the chain length ($N \approx 100$), we can anticipate corrections to $\mathrm{d}\ln C/\mathrm{d}T$ of the same order of magnitude as that previously reported for $\mathrm{d}\ln \Delta\alpha^*/\mathrm{d}T$.[5-7] Moreover, this contribution to $\mathrm{d}\ln \Delta\alpha^*/\mathrm{d}T$ persists for networks swollen with optically isotropic solvents (see eq 16 with $\Delta\alpha' = 0$ and finite ϕ).

Concluding Remarks

In the past, investigators using a variety of experimental techniques[4-7,16,41] concluded that short-range orientational correlations may play an important role in the physicochemical properties of strained elastomers. We have demonstrated that ^2H NMR provides a means for probing short-range nematic-like order in strained elastomers. The phenomenological lattice description of the orientational order of swelling agents in strained elastomers articulates the role of the nematic-like interactions in a formulation that is readily extended to opticoelastic behavior. We obtain an expression for the birefringence of swollen networks (eq 13 and 14) wherein there are three contributions: the intrinsic segment anisotropy, segment–segment correlations, and segment–solvent interactions; these terms parallel the three contributions to the birefringence intuited by Bullough some 20 years ago.[42] In general, our findings emphasize that the presence of nematic-like interactions in highly swollen networks complicates the extraction of intrinsic characteristics of isolated chains ($\mathrm{d}\ln \Delta\alpha^*/\mathrm{d}T$) from stress–optical data, and this complication persists irrespective of the nature of the swelling agent.

Finally the power of the ^2H NMR technique is apparent in this study. It obviates the perturbative disadvantages characteristic of conventional probe techniques (electron spin resonance and fluorescence) while providing a microscopic picture of local changes in the elastomer. A zero-order approximation to the local response of the network chain under deformation may be inferred from the ^2H NMR of flexible swelling agents such as the *n*-heptane-d_{16} (Figure 2). One of us has recently presented a scheme for deriving the orientational order of flexible probes from the quadrupolar splittings.[43] Obviously, the chain behavior can be monitored directly with ^2H NMR and we are currently extending this technique to deuterium labels at specific sites on the network chains. For a judicious choice of a labeled elastomer, it should be possible to compare in a complementary manner the short-range segmental behavior derived from ^2H NMR with long-range configurational behavior ascertained from neutron scattering[44] and thereby obtain a complete picture of the response of the network to external constraints.

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(39) The quadrupolar splitting for $CDCl_3$ shown in Figure 2 yields a value of S_{zz} that is a factor of 1.5 larger than that observed for C_6D_6 (after including the differences in θ_i and $(e^2qQ/h)_i$) constrained in the same network under the same conditions ($\lambda = 2$, $\phi = 0.5$).

(40) For solvents (segments) with less than C_3 symmetry, specification of the average orientation of the molecule relative to the constraint requires more than one element of the order matrix **S**. In principle, only two parameters are necessary (if **S** is diagonalized) but, in practice, the property considered is usually a tensor (α) and is not always diagonal in the frame that diagonalizes **S**. In general, the polarizability along the constraint direction α_{zz} is given by $\alpha_{zz} = {}^1/_3 \operatorname{Tr} \alpha + {}^2/_3 \sum_{\alpha,\beta}^{xyz} \alpha_{\alpha\beta} S_{\alpha\beta}$.

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Carbon-13 Nuclear Magnetic Resonance Studies of Solid Segmented Copolymers. 1. Mobile Domains of a Polyester Thermoplastic Elastomer

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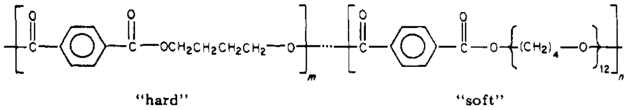
ABSTRACT: ^{13}C NMR was used to characterize the molecular motions which occur in the mobile regions of solid Hytrel thermoplastic elastomer, a segmented copolymer composed of tetramethylene terephthalate "hard" segments and poly(tetramethyleneoxy) terephthalate "soft" segments. The samples studied range from 0.96 to 0.80 mole fraction hard segments. Proton scalar decoupled ($\gamma H_2/2\pi$ = 4 kHz or 1 G) ^{13}C NMR spectra were observed in the solid state for all Hytrel samples but not for the poly(butylene terephthalate) homopolymer. The fraction of each sample which contributes to the scalar-decoupled spectrum was found to consist of all of the aliphatic carbons of the soft segments and ~10% of the terephthalate and hard-segment carbons. The soft-segment aliphatic carbon line widths are a linear function of the average hard block length of the polymer but are essentially independent of temperature over the range 30–110 °C. The T_1 values are identical for both soft-segment aliphatic carbons and are independent of the mole fraction of hard segment in the polymer. The T_1 values increase with increasing field strength and with increasing temperature. The NOE values at 47 kG for the soft-segment OCH_2 and $CH_2CH_2CH_2CH_2$ carbons are also independent of the hard-segment content of the polymer. Taken together, these data indicate that the part of the dipolar Hamiltonian made time dependent by anisotropic thermal motion is independent of the hard-segment content of the polymer. However, the angular range over which reorientation occurs is directly related to the average hard block length. These results support a model for Hytrel structure in which there is phase separation and in which there is negligible mixing of the two phases at the domain boundaries.

Introduction

Block copolymer thermoplastic elastomers generally contain amorphous "soft" segments and structured "hard" segments which are not miscible. The chemical incompatibility of the two segments results in phase separation, from which the unique mechanical and thermal properties of these polymers derive. The soft segments impart elastomeric character to the polymers, whereas the hard segments form thermally reversible noncovalent networks analogous to the covalent cross-links in elastomers. The hard-segment networks rely on various intramolecular interactions for their stability: the hard segments of the polyurethanes are stabilized by hydrogen bonding,[1] the styrene–butadiene or –isoprene block copolymer hard segments contain polystyrene in the glassy phase,[2] the ionomer resins rely upon ion clusters in the hard phase for their structural stability,[3,4] and the polyester hard segments form a network of crystalline lamellar regions.[5]

Although the nature of the microphase separation,[6] the dynamic interactions between the chains in the hard and soft phases,[2,7,8] and the composition of the domain boundaries[9] in the polyurethanes, the polystyrene–butadiene, and the polystyrene–isoprene systems have been the subjects of recent active study, the polyester class of block copolymers seems to have escaped a similar systematic examination.[5]

Hytrel is a thermoplastic polyester elastomer produced by E. I. du Pont de Nemours and Co. and is available in a range of compositions of *m* tetramethylene terephthalate hard segments and *n* poly(tetramethyleneoxy) terephthalate soft segments.



Hytrel is formed by the melt transesterification of dimethyl terephthalate, 1,4-butanediol, and poly(tetramethylene ether) glycol, the latter having a number-average molecular weight of about 1000.[10] The distribution of the copolymer blocks is assumed to be random.[5,11]

Electron microscopy has shown that these copolymers exhibit a two-phase morphology.[5,12,13] However, the structure consists of continuous and interpenetrating crystalline and amorphous phases,[5] rather than the discrete domain structure which is seen for styrene–butadiene or

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