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DEUTERIUM MAGNETIC RESONANCE STUDY OF STRAINED SWOLLEN CROSSLINKED ELASTOMERS

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ABSTRACT

The ^{2}H NMR of uniaxially elongated swollen crosslinked natural rubber and butadiene-styrene copolymer samples swollen with C_6D_6 and C_6D_5CD, are studied in this paper. The lines of each inequivalent deuteron are split into doublets due to the interaction between the quadrupole moment of the deuteron and the electric field gradient from the interaction between chain segments. One orientational order parameter is enough for each of these two swelling agents. From the slopes and intercepts obtained from a plot of log $[\Delta\nu_i/(\lambda^2 - \lambda^{-1})]$ against log $(G^{-1}\phi^{2/3})$, the relative number N of chain segments between the crosslinks for different crosslink densities can be estimated. The results obtained are in good agreement with each other and with results calculated from the Flory equation. Our data show that the "random-walk statistical model" better represents the low or moderate crosslink density samples.

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INTRODUCTION

In the past few years there has been considerable interest in the deuterium NMR study of uniaxially strained elastomers [1-4]. Deuterated swelling agents exhibit quadrupolar splittings which have an explicit dependence on the extension ratio, the degree of swelling, and the temperature. The existence of short-range nematiclike segmental order has already been confirmed indirectly by some experiments.

In this paper we study the ^{2}H NMR of uniaxially strained natural rubber and butadiene-styrene copolymers in order to explore the relation between the crosslink density and the number of chain segments between crosslinks. Rubbers with different crosslink densities and different swelling agents are used. We find that the induced orientational order increases with crosslink density, as predicted by the kinetic theory of rubber elasticity. The results obtained with different swelling agents are consistent. Following the theory developed by Deloche and Samulski based on the de Genne's lattice model, one can estimate the relative number of chain segments between crosslinks, which are in good agreement for two swelling agents and with estimates obtained with the Flory equation [5]. It is also suggested that one order parameter is enough for the nonsymmetrical swelling agent $C_6D_5CD_3$ although it may exhibit anisotropic reorientational diffusion in the deformed rubber network.

EXPERIMENTAL

Natural rubber samples containing 4.6% zinc oxide and 2.1% sulfur are cured at 156°C and 120 kg/cm^2. Samples with different crosslink densities are obtained by changing the curing time. Crosslinked butadiene-styrene copolymers are prepared in a similar way. By swelling the samples in CCl_4 at room temperature, one can characterize each sample by a value ϕ_{eq}, which is the volume fraction of the polymer at the swelling equilibrium. The values obtained are 0.1344, 0.1377, 0.1708, and 0.1743 for the natural rubber samples, and 0.1650 and 0.2166 for the butadiene-styrene copolymers. Higher ϕ_{eq} values correspond to higher crosslink densities. Samples are cut into strips of 23 X 1.8 X 1.0 mm. Deuterobenzene (C_6D_6) and deuterotoluene ($C_6D_5CD_3$) are used as swelling agents. A glass tube for holding the samples uniaxially elongated is inserted into a 5-mm NMR sample tube. One end of the sample is fixed to the bottom of the inserted tube and the other end is fixed by a thread passing through the center of the cap for extension. The volume fraction of rubber, ϕ, is calculated by weighing the samples before and after swelling according to the formula

$V_{\text{rubber}}/(V_{\text{rubber}} + V_{\text{solvent}})$. The extension ratio, λ, is determined by $\lambda = L/L_0$, where L and L_0 are, respectively, the strained and unstrained lengths of the swollen elastomer. The deuterium resonance is observed at 12.211 MHz by using an external deuterium lock in a Varian FT-80A NMR spectrometer.

THEORY

When a swollen crosslinked elastomer is uniaxially deformed, the orientational distribution of chain segments changes to a new equilibrium distribution. This new distribution establishes a short-range nematiclike segmental order and produces a nonzero partially averaged electric field gradient (efg) in the network. The interaction between the quadrupole moment of the deuteron and the efg raises the degeneracy of the three Zeeman levels. Hence, each of the nonequivalent deuterons in the swelling agent will exhibit a doublet and the ^{2}H-NMR spectrum becomes a superposition of these discrete doublets. In the case of deuterated molecules with high symmetry, the quadrupole splitting is directly related to the S_{zz} order parameter, which is the zz component of the symmetric traceless orientational order tensor $\hat{S}$. For deuterated molecules of lower symmetry, generally more than a one order parameter is necessary unless special conditions are fulfilled.

When a one order parameter is enough to describe the system, the relationship between $\Delta\nu_i$ and the extension ratio λ is as follows [6-8]:

$$\Delta\nu_i = \frac{c_i g}{2} \frac{G}{N\phi^{2/3}} (\lambda^2 - \lambda^{-1}), \tag{1}$$

$$c_i = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)_i P_2(\cos\Omega) P_2(\cos\theta_i), \tag{2}$$

where $(e^2qQ/h)_i$ is the static quadrupole coupling constant of the ith deuteron, P_2 is the second Legendre polynomial, Ω is the angle between the constraint **d** and the magnetic field **H**, θ_i is the angle between the ith C–D bond and the principal axis of the molecule, N is the number of chain segments between crosslinks, g is a proportionality factor which depends on the nature of the elastomer and the physicochemical properties of the swelling molecule, and G is an enhancement factor which represents the enhancement of segmental orientation order due to the presence of the nematiclike interaction between the chain segments in real systems. The enhancement factor G should be closely related to the volume fraction, but the explicit relationship depends on the different statistical models.

Tanaka and Allen [9] derived the following expression for G:

$$G = \left[\frac{4e(3 - \phi)}{q\phi} - 1 \right]^{-1}, \tag{3}$$

where e equals 9/4 for the random-walk model and 27/8 for the restricted-walk model. We can rewrite Eq. (1) as

$$\log\left(\frac{\Delta\nu_i}{\lambda^2 - \lambda^{-1}}\right) = \log\left(\frac{c_i g}{2}\right) - \log N - \log\,(G^{-1}\phi^{2/3}). \tag{4}$$

If the correct $G(\phi)$ is chosen, a straight line will be obtained when $\log\,[\Delta\nu_i/(\lambda^2 - \lambda^{-1})]$ is plotted against $\log\,(G^{-1}\phi^{2/3})$. The slope of this line should equal -1 and its intercept should equal $I = \log\,(c_i g/2) - \log N$. If an incorrect $G(\phi)$ function is chosen, we might not obtain a straight line or we might obtain a nearly straight line with a different slope. This provides a method to test the different models on the assumption that g remains constant for samples of different crosslink density. For a fixed ϕ, the ratio of N can be estimated from one of the following two equations:

$$\log\left(\frac{N_b}{N_a}\right) = \log\left(\frac{\Delta\nu_i}{\lambda^2 - \lambda^{-1}}\right)_a - \log\left(\frac{\Delta\nu_i}{\lambda^2 - \lambda^{-1}}\right)_b \tag{5}$$

or alternatively

$$\log\left(\frac{N_b}{N_a}\right) = I_a - I_b. \tag{6}$$

RESULTS

When C_6D_6 is used as the swelling agent in the undeformed state ($\lambda = 1$), a single line appears, which indicates that the medium is isotropic. When these samples are uniaxially elongated, this line splits into a symmetrical doublet resulting from the quadrupole interaction between the deuteron and the efg. The splitting $\Delta\nu_i$ increases with the extension ratio λ for a fixed volume

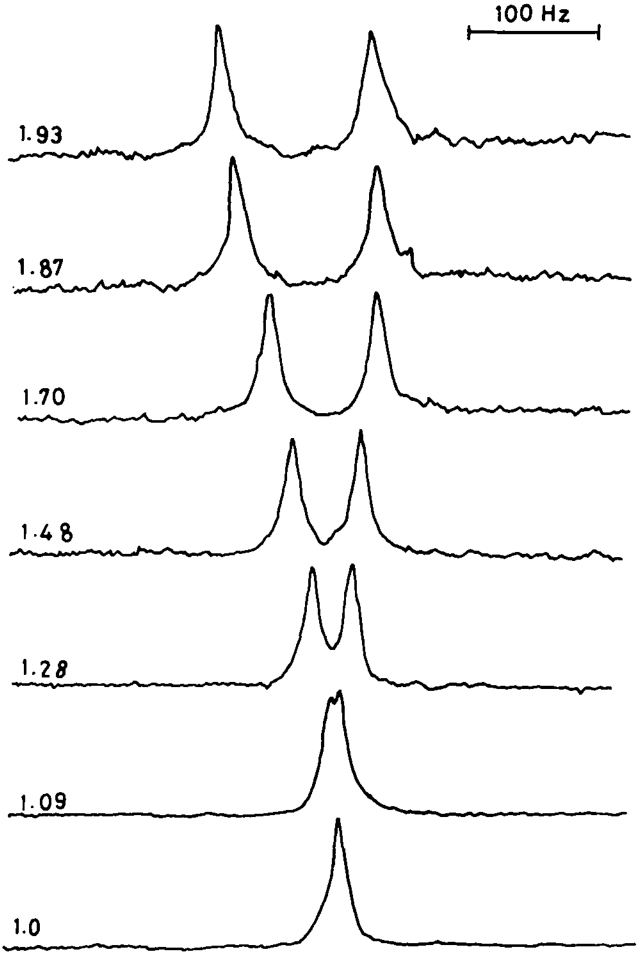


FIG. 1. ^{2}H NMR of C_6D_6 in uniaxially elongated, swollen, crosslinked natural rubber (ϕ_{eq} = 0.1743, ϕ = 0.547). Numbers on the spectra are λ values.

fraction ϕ. A representative result is shown in Fig. 1. If we plot $\Delta\nu_i$ against $\lambda^2 - \lambda^{-1}$ for fixed ϕ, straight lines pass through the origin at small or moderate λ as shown in Fig. 2.

When $C_6D_5CD_3$ is used as the swelling agent, two signals appear in the

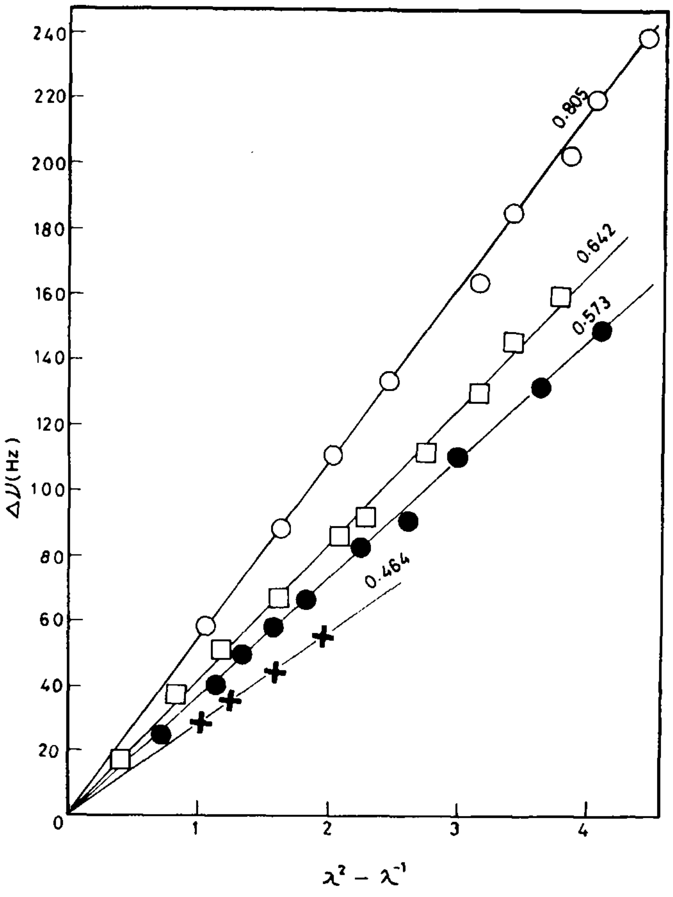


FIG. 2a. Plots of $\Delta\nu$ against $\lambda^2 - \lambda^{-1}$. Numbers on the lines are ϕ values. Swelling agent: C_6D_6. Natural rubber ($\phi_{eq} = 0.1743$).

undeformed state, one for CD_3 deuterons and the other for the deuterons in the benzene ring. When the samples are uniaxially elongated, each line splits into a doublet. At high λ, an extra small doublet appears, which belongs to the *para* deuteron in the benzene ring since there is a bigger difference in θ_i between the *para* and the *ortho* and *meta* deuterons. Representative spectra of $C_6D_5CD_3$ swelling are shown in Fig. 3. Only the *ortho*, *meta*, and CD_3

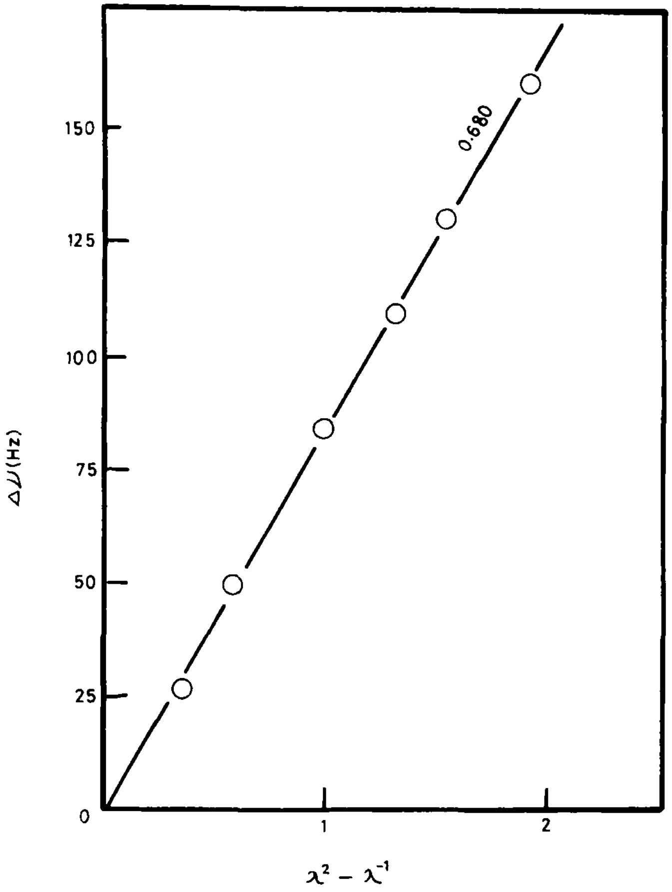


FIG. 2b. Plot of $\Delta\nu$ against $\lambda^2 - \lambda^{-1}$. Number on the line is the ϕ value. Swelling agent: C_6D_6. Butadiene-styrene copolymer ($\phi_{eq} = 0.165$).

doublets are considered. Their quadrupole splittings are represented by $\Delta\nu_2$ and $\Delta\nu_1$, respectively. When we plot $\Delta\nu_2$ or $\Delta\nu_1$ against $\lambda^2 - \lambda^{-1}$, we obtain a series of straight lines passing through the origin (Fig. 4). It is interesting to point out that, if $\Delta\nu_2$ is plotted against $\Delta\nu_1$ for samples with different ϕ_{eq} values, the points are located on a straight line passing through the origin (Fig. 5).

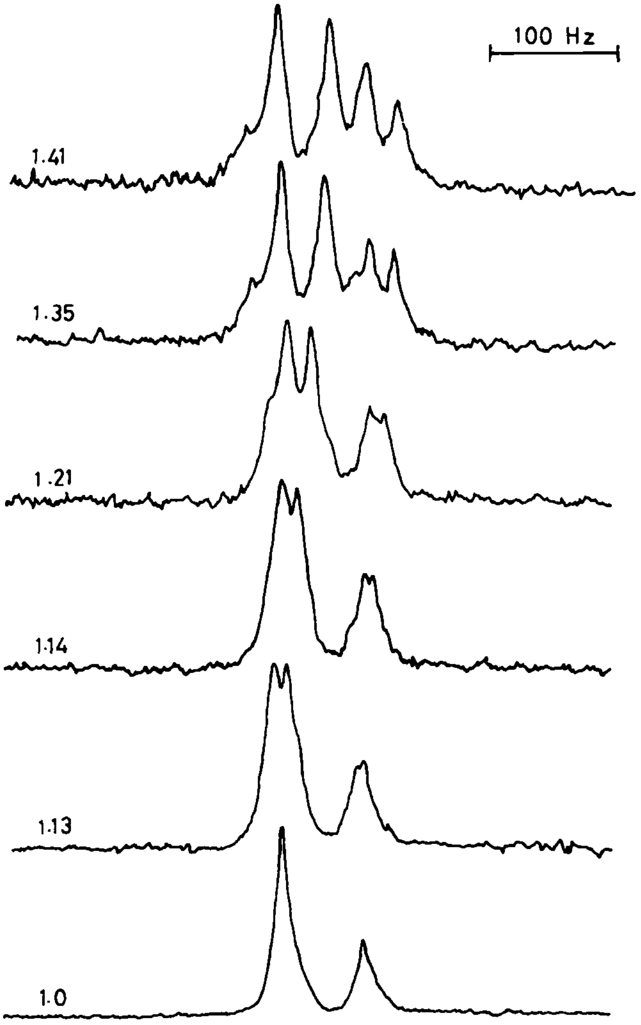


FIG. 3. ^{2}H NMR of $C_6D_5CD_3$ in uniaxially elongated, swollen, cross-linked natural rubber (ϕ_{eq} = 0.1743, ϕ = 0.477). Numbers on the spectra are λ values.

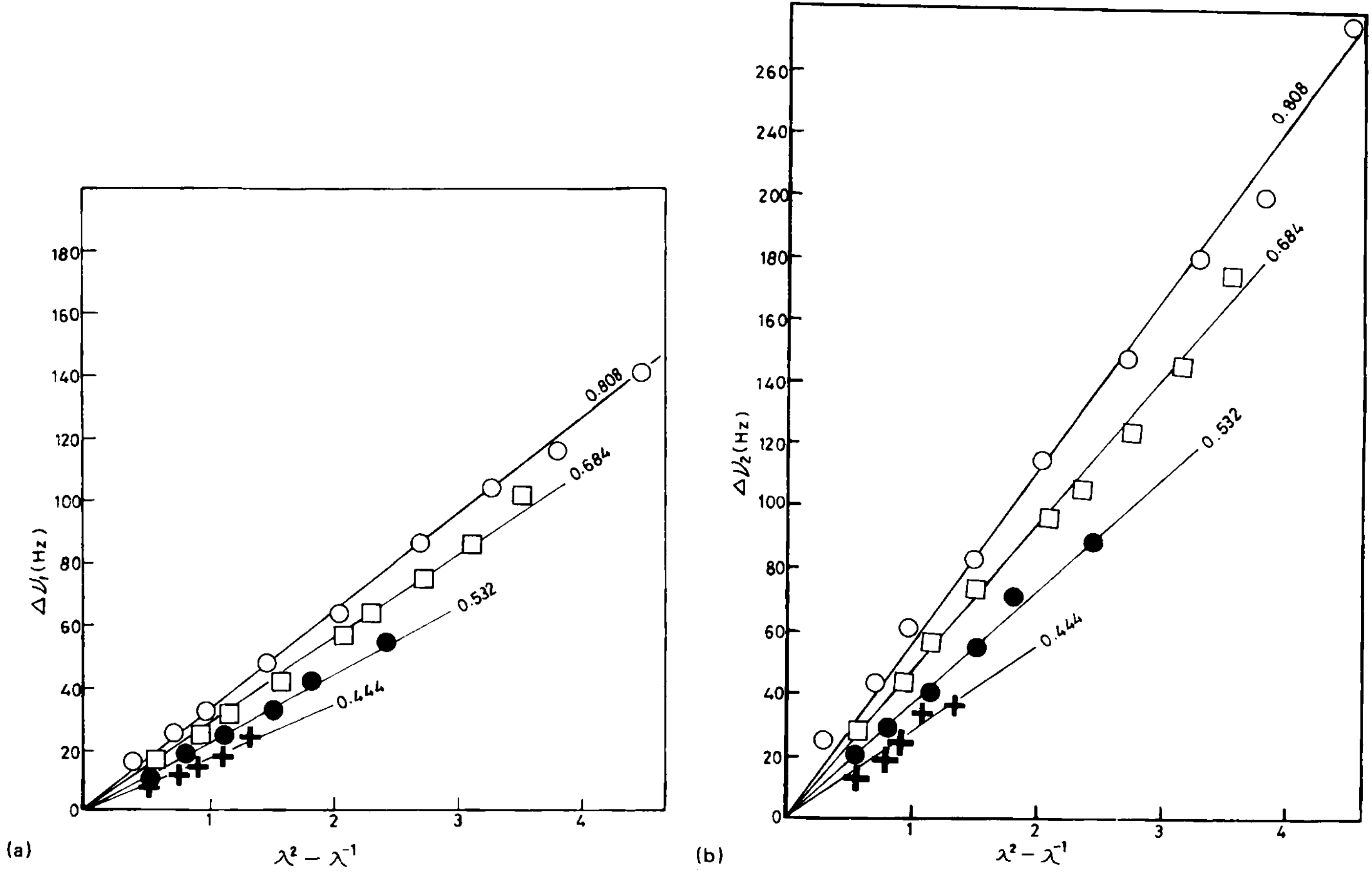


FIG. 4. Plots of $\Delta\nu_1$ (a, left) and $\Delta\nu_2$ (b, right) against $\lambda^2 - \lambda^1$. Numbers on lines are ϕ values. Swelling agent: $C_6D_5CD_3$. Sample: Natural rubber ($\phi_{eq} = 0.1743$).

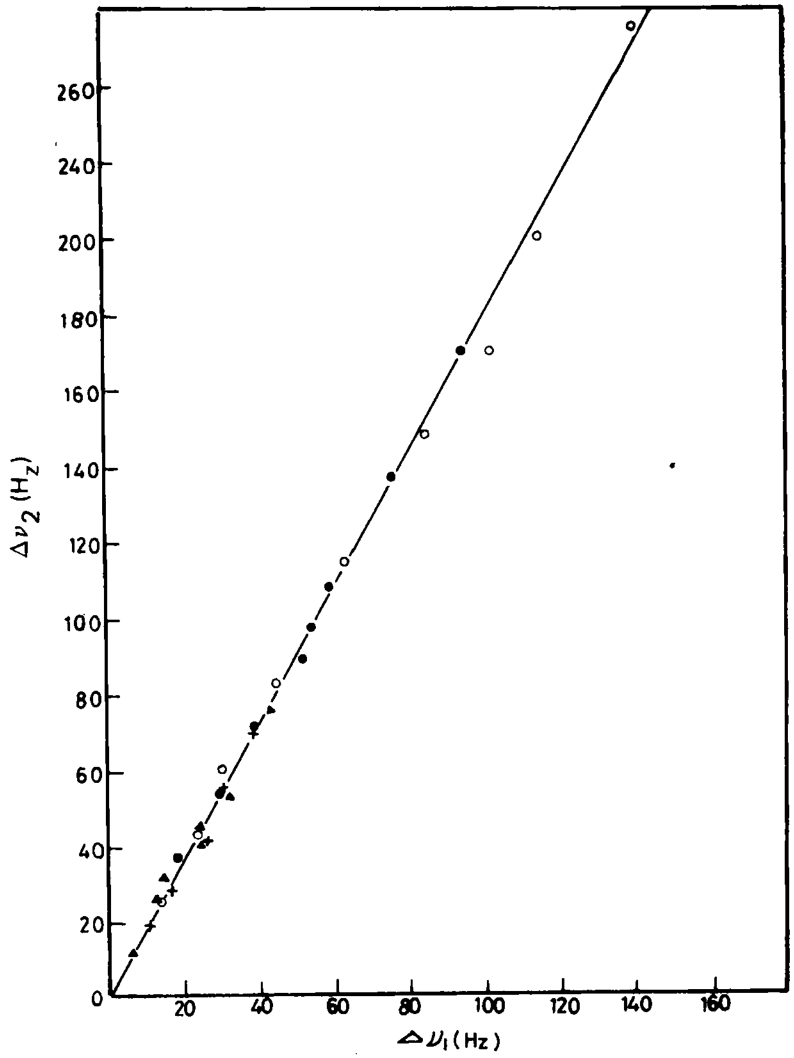


FIG. 5. Plot of $\Delta\nu_1$ against $\Delta\nu_2$. Swelling agent: $C_6D_5CD_3$. Sample: Natural rubber. $\phi_{eq} = 0.1743$ (○ = 0.808, + = 0.532). $\phi_{eq} = 0.1344$ (● = 0.815, ▲ = 0.533).

DISCUSSION

The origin of the doublet splittings has been explained. In the uniaxially deformed swollen crosslinked rubber network, there is a nematiclike orientational field arising from the short-range interaction between partially aligned chain segments. Doublet splittings result from the interaction between the efg generated in this nematic field and the quadrupole moment of the deuterons. The symmetry of the intensity of the doublet lines indicates that the orientational field in the vicinity of the deuteron is uniaxial.

Owing to the C_6 symmetry of the C_6D_6 molecule, it is not surprising that only a one order parameter S_{zz} is necessary to describe the system. However, for the $C_6D_5CD_3$ molecule, the symmetry is lower than for C_6D_6 and it is not evident whether one parameter is enough to describe this system. But, according to the discrimination condition proposed by Dong et al. [10], a straight line passing through the origin when $\Delta\nu_2$ is plotted against $\Delta\nu_1$, as in Fig. 5, indicates that a one order parameter is sufficient to describe the $C_6D_5CD_3$ system. Therefore, all the equations listed above are still valid.

Using the results of four natural rubber samples and two butadiene- styrene copolymers, we have tested the validity of Eq. (4). We find that, if we use the random-walk model, $e = 9/4$, the slopes of the straight lines obtained are very close to -1, while if we use the restricted-walk model, $e = 27/8$, the slopes of the lines become -1.4 with a poorer correlation coefficient. An example of the use of linear regression analysis to test different models is shown in Table 1. From this table it is concluded that the random-walk model is a better representation for low or moderate crosslink densities.

Finally, we can calculate the ratio of N from the slopes and intercepts in Fig. 6 according to Eq. (5) or Eq. (6). The results are listed in Table 2.

TABLE 1. Linear Regression Analysis of the Plot of log $[\Delta\nu_i/(\lambda^2 - \lambda^{-1})]$ against log $(G^{-1}\phi^{2/3})$[a]

Model	Correlation coefficient	Slope	Intercept
Random walk	-0.9846	-1.156	1.7636
Restricted walk	-0.9766	-1.417	2.1596
Deloche Samulski ($G = \phi^2$)	-0.9965	-0.956	1.6884

[a] Sample, $\phi_{eq} = 0.1344$; swelling agent, C_6D_6.

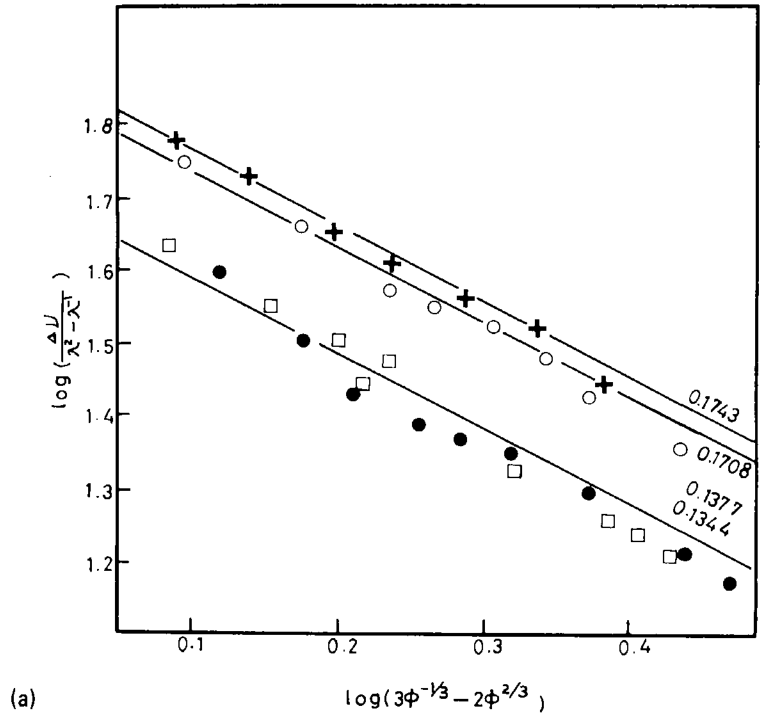
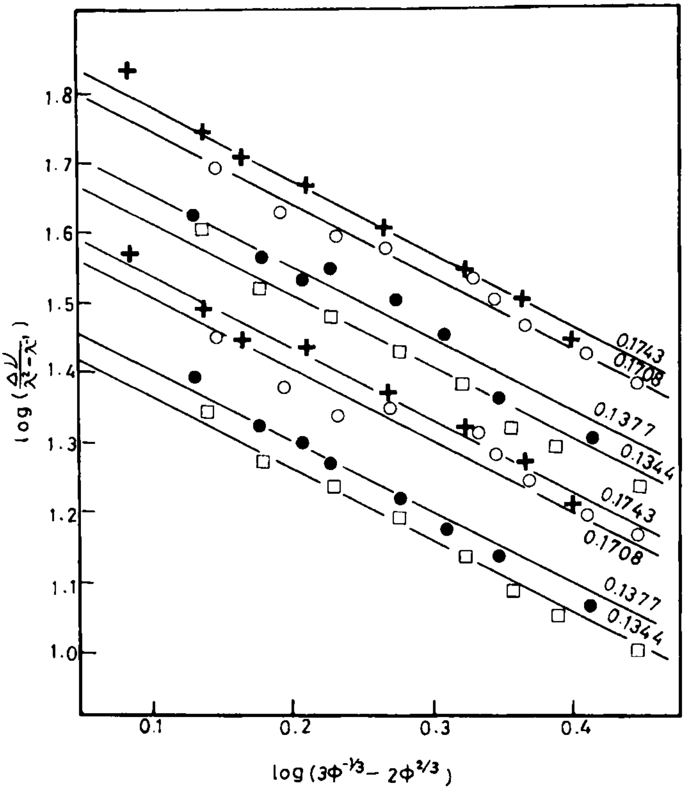
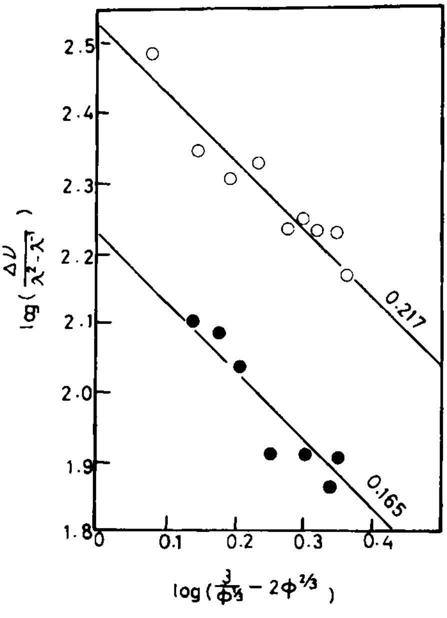


FIG. 6. (a) Plots of log $[\Delta\nu_1/(\lambda^2 - \lambda^{-1})]$ against log $(3\phi^{-1/3} - 2\phi^{2/3})$. Numbers on the lines are ϕ_{eq} values. Sample: Natural rubber. Swelling agent: C_6D_6. (b) Plots of log $[\Delta\nu_i/(\lambda^2 - \lambda^{-1})$ against log $(3\phi^{-1/3} - 2\phi^{2/3})$. Numbers on the lines are ϕ_{eq} values. Sample: Natural rubber. Swelling agent: $C_6D_5CD_3$. Upper four lines refer to $\Delta\nu_2$. Lower four lines refer to $\Delta\nu_1$. (c) Plots of log $[\Delta\nu_i/(\lambda^2 - \lambda^{-1})$ against log $(3\phi^{-1/3} - 2\phi^{2/3})$. Numbers on the lines are ϕ_{eq} values. Sample: Butadiene-styrene copolymer. Swelling agent: C_6D_6.


1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.1
0.2
0.3
0.4
$\log\left(\frac{\Delta\nu}{\lambda^2-\lambda^{-1}}\right)$
$\log(3\phi^{-1/3}-2\phi^{2/3})$
0.1743
0.1708
0.1377
0.1344
0.1743
0.1708
0.1377
0.1344

(b)


2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
0
0.1
0.2
0.3
0.4
$\log\left(\frac{\Delta\nu}{\lambda^2-\lambda^{-1}}\right)$
$\log\left(\frac{3}{\phi^{1/3}}-2\phi^{2/3}\right)$
0.217
0.165

(c)

TABLE 2. Relative Number of Chain Segments between Crosslinks Estimated from Eq. (5) or Eq. (6)[a]

	Sample					
	Natural rubber				Butadiene-styrene copolymer	
ϕ_{eq}	0.1743	0.1708	0.1377	0.1344	0.2166	0.1650
C_6D_6	1	1.09	1.45	1.45	1	1.97
$C_6D_5CD_3$	1	1.06	1.32	1.45		
Flory equation	1	1.02	1.46	1.50	1	1.68

[a] Two sets of data can be obtained from the $C_6D_5CD_3$ swelling agent, one from $\Delta\nu_2$ and the other from $\Delta\nu_1$. The results are the same since a linear relationship exists between $\Delta\nu_2$ and $\Delta\nu_1$.

For comparison, we also calculate these ratios by the Flory equation

$$\ln(1-\nu_2)+\nu_2+\chi\nu_2^2+\frac{\rho V_1}{M_c}(\nu_2^{1/3}-\nu_2/2)=0, \tag{7}$$

where V_1 is the molar volume of the swelling agent, ν_2 is the volume fraction of polymer, ρ is the density in the unswollen state, M_c is the number-average chain molecular weight, and χ is the Flory-Huggins polymer-solvent interaction parameter.

It is evident that the results obtained from swelling agents are in good agreement with each other and with the Flory equation.

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