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DEUTERIUM NMR OF STRAINED SWOLLEN CROSSLINKED ELASTOMERS: EFFECT OF CROSSLINK DENSITY ON THE ORIENTATIONAL ORDER OF CHAIN SEGMENTS†

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ABSTRACT

The ^2H NMR of uniaxially strained swollen chloroprene rubbers and butadiene-styrene copolymers with different crosslink densities is studied. The relative number of chain segments between crosslinks of various samples is obtained. The results are in approximate agreement with those obtained from the Flory equilibrium-swelling method. It is found that the enhancement factor G depends not only on the lattice-walk model and swelling of rubber, such as Tanaka etc. expected, but also on the crosslink density and the structure of the rubber. The formula relating G to the number of chain segments between crosslinks is derived from theory. Moreover, we can also estimate the relation between the enhancement factor G_r of real rubber and G calculated from the theory of the lattice model. The ^2H NMR results of these samples indicate that the interaction between chain segments decreases with increasing crosslink density.

INTRODUCTION

Until recently, experimental investigations of rubbers mainly dealt with measurements of elasticity and optical elasticity. Both types of studies revealed some deviations from the kinetic description of rubber elasticity based on volumeless Gaussian chains [1-4]. Some of these deviations

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have often been ascribed to correlation between chain segments in the deformed network [5, 6]. The question "How does the macroscopic strain affect the chain behavior?" has led to controversial discussion. This is the reason that various microscopic techniques are currently being used to examine elastomeric chains under deformation [7]. Among these techniques, deuterium magnetic resonance (^{2}H NMR) is well adapted for probing local ordering. In the past a few years, ^{2}H NMR systematic studies on constrained swollen network have shown that deuterated swelling agents exhibit quadrupolar splittings that depend explicitly on the extension ratio, the degree of swelling, the crosslink density, and the temperature [8–11]. The quadrupolar splittings were correlated with the orientational order generated in uniaxially deformation of rubber. Although the question "How does the crosslink density affect the orientational order?" has been studied, an adequate relation between them has not been obtained.

In this paper, the ^{2}H NMR of uniaxially strained, swollen, crosslinked chloroprene rubbers and butadiene–styrene copolymers with different crosslink densities is studied by means of C_6D_6.

EXPERIMENTAL

Chloroprene rubber and butadiene–styrene copolymer were cured at 143 and 150°C, respectively. The different densities were controlled by changing the sulfur level and the curing time. The crosslink density is characterized by ϕ_{eq}, which is the volume fraction of rubber at swelling equilibrium at room temperature. Chloroprene rubbers and butadiene–styrene copolymers were swollen in C_6H_6 and in CCl_4, respectively. Both are good solvents for the corresponding rubber. Table 1 includes the results and an estimation of the mean molecular weight ($\overline{M}_c$) between crosslinks calculated from the Flory equation [16] by the corresponding value of ϕ_{eq}.

Samples were cut into strips of 25 × 2.5 × 1.0 mm. Deuterobenzene (C_6D_6) was used as the swelling agent. The constrained direction was parallel with the tube and was perpendicular to the external magnetic field. The method of elongation can be seen in our previous paper [9]. The volume fraction of rubber was calculated by the weighting method. The extension ratio λ was determined from $\lambda = L/L_0$, where L and L_0 are the strained and unstrained lengths of swollen elastomer, respectively.

The deuterium magnetic resonance was observed at 12.211 MHz with a Varian FT-80A NMR spectrometer. An external deuterium lock was used. The sample tube was not spinning.

TABLE 1. Characterization of Cured Crosslinked Chloroprene Rubber and Butadiene-Styrene Copolymer

Polymer	Sample number	ϕ_{eq}	$\overline{M}_c$
Chloropene rubber	1	0.056	54,300
	2	0.069	35,600
	3	0.117	14,400
	4	0.134	10,300
	5	0.135	10,300
Butadiene-styrene copolymer	1	0.030	293,000
	2	0.062	75,300
	3	0.080	44,300
	4	0.109	24,400
	5	0.120	21,000

THEORY

When the crosslinked swollen elastomer is uniaxially deformed, chain segments become oriented. It is considered that the orientational order originates in part from that anticipated by an affine deformation of the isolated chains and, in another part, from short-range interactions between the partially aligned chain segments [13]. The probe can be used as the swelling agent to measure indirectly the orientational order generated by the interactions between chain segments. For a deuterated probe of high symmetry, the quadrupole splitting can be related to the orientation-order parameter *S*, which characterizes the enhancement of the orientational order of segments due to the interaction between them. From this, the relation among the splitting $\Delta\nu$ of the deuterated probe, the extension ratio λ, and the volume fraction of rubber ϕ is established in the lattice model of a rubber network [9] as follows:

$$\Delta\nu = (2N)^{-1} gBG\phi^{-2/3}(\lambda^2 - \lambda^{-1}), \tag{1}$$

$$B = (2/3)(e^2qQ/h)P_2(\cos \Omega)P_2(\cos \theta), \tag{2}$$

where e^2qQ/h is the static quadrupole coupling constant, P_2 is the second Legendre polynomial, Ω is the angle between the strain direction and the magnetic field, θ is the angle between the C—D bond and the *z*-axis of the probe molecule, g is the interaction parameter of the probe with the segments, N is the number of equivalent random links between crosslinks, and G is the enhancement factor. The latter represents the relative increase of segmental orientational order due to the presence of the nematic-like interaction between the chain segments; it is lattice-model dependent. According to Flory's analysis [18] of the entropy of fusion of various polymer crystals, the three-dimensional simple cubic lattice (i.e., the coordination number Z is equal to 6) appears to be the best choice, or at least, a representative one. On the basis of this model, G may be expressed by a semitheoretical equation as follows [17] :

$$G = [f(3 - \phi)/(\phi - 1]^{-1}, \tag{3}$$

where f is a constant. In the Appendix we derive the expression for f according to the method of Tanaka and Allen [17]. We differ from their method in that we retain the second-order small term $(x/Nb)^2 = 1/N$ in the derivation, which leads to

$$f = f_0 + a/N. \tag{4}$$

We can rewrite Eq. (4) as

$$f = f_0 + (aq'/N_m{}^*)r^{-1}, \tag{5}$$

where f_0 is a constant which depends on the random-walk model of the chain; a is also a constant; q' is the number of monomers per equivalent random link, a measure of chain "stiffness" or "flexibility"; $N_m{}^*$ is the number of monomers between crosslinks of a designated sample; and r is the ratio of N_m to $N_m{}^*$. We can rewrite Eq. (1) as

$$\log [\Delta\nu/(\lambda^2 - \lambda^{-1})] = \log (gB/2) - \log (N) - \log (G^{-1}\phi^{2/3}). \tag{6}$$

The parameter f in G (see Eq. 3) is adjusted until the slope of the straight line of $\log [\Delta\nu/(\lambda^2 - \lambda^{-1})]$ vs $\log (G^{-1}\phi^{2/3})$ is -1. From the intercept of the straight lines, we can obtain the relative N through the following equation:

$$\log (N/N^*) = I^* - I. \tag{7}$$

If q' is approximately equal for two different crosslink densities, the relative N is the same as the relative N_m, i.e.,

$$r = N_m/N_m^* = N/N^*. \tag{8}$$

RESULTS

Figure 1(a) shows how the ^{2}H-NMR spectrum of deuterobenzene in a chloroprene rubber network changes as the sample is elongated uniaxially from a single line in the relaxed state ($\lambda = 1$) to quadrupolar doublets ($\lambda > 1$). The splitting increases with the extension ratio for a fixed volume fraction. Similar spectra were obtained for butadiene–styrene copolymer (Fig. 1b). Plots of $\Delta\nu$ against $\lambda^{-2} - \lambda^{-1}$ in Fig. 2 are seen to be straight lines passing through the origin for both polymers. The slopes of the straight lines of $\log[\Delta\nu/(\lambda^2 - \lambda^{-1})]$ against $\log(G^{-1}\phi^{2/3})$ are all made equal to -1 by adjusting f, as shown in Fig. 3. The ratios of N_m are then estimated from the intercepts of the straight lines in Fig. 3, according to Eq. (7) and Eq. (8). The results are listed in Table 2 together with the relative ratios of $\overline{M}_c$

DISCUSSION

We focus here on the analysis of the effect of crosslink density and on the interaction between chain segments. We also discuss the common use and reliability of Eq. (6) when the parameter f is used in G.

Figure 2 shows that the slopes of the lines decrease with ϕ. The reason is that interaction between chain segments decreases with an increasing number of solvent molecules around the chain segments.

How about the quantitative relation between G and ϕ? Deloche et al. obtained the relation $G \propto \phi^2$. Study of natural rubber showed that it can be described by the random-walk model, i.e., $f = 1$ in Eq. (3). These results show that the changes of the enhancement factor G with ϕ are not the same for different kinds of rubber. For chloroprene rubber and butadiene–styrene copolymer, G depends not only on ϕ but also on the crosslink density. If G is used in the parameter form, such as in Eq. (3), various effects (crosslink density, type of rubber, etc.) will be included in f. Hence, we can obtain a relation between $\Delta\nu$ and ϕ (Eq. 6), which is in common

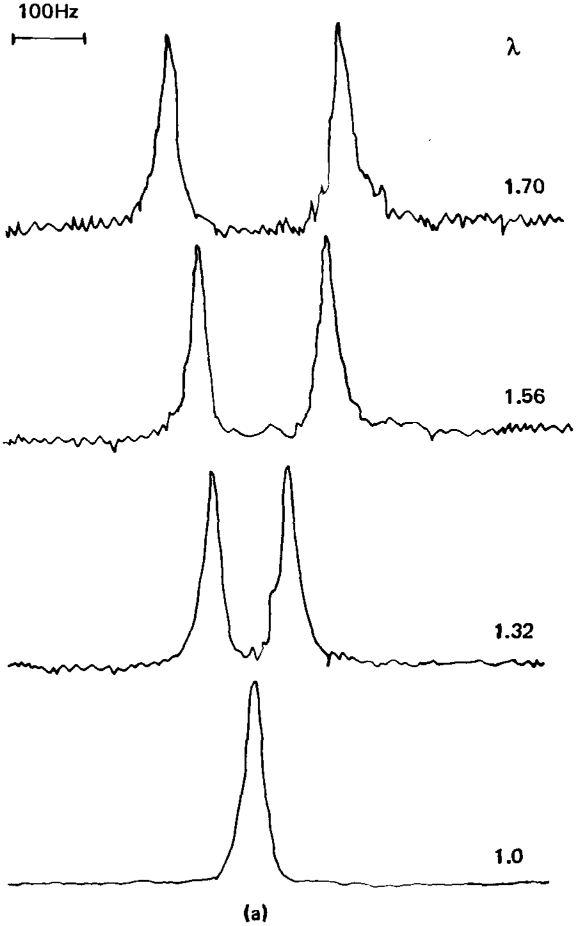
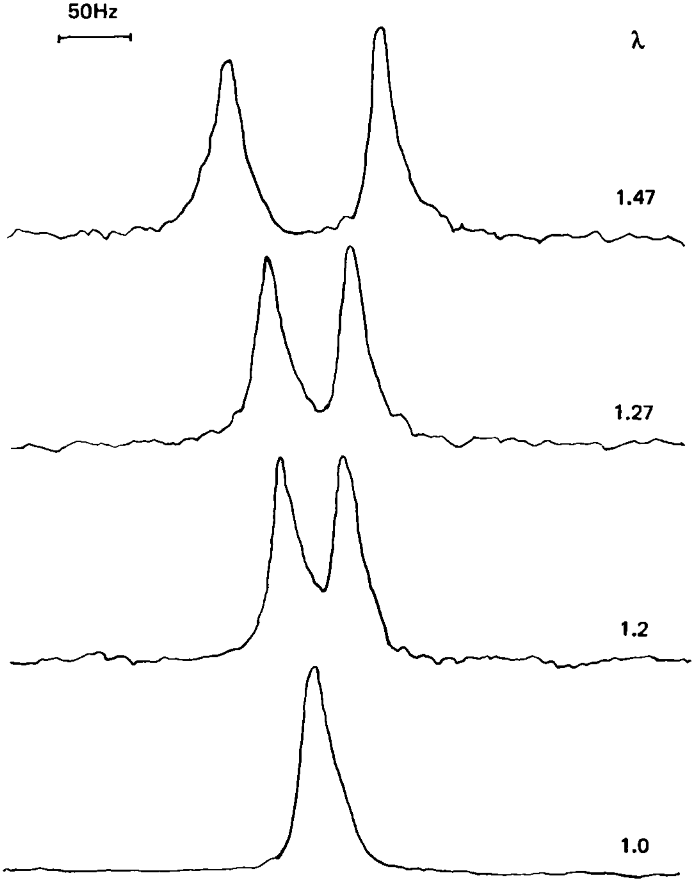


FIG. 1. ^{2}H-NMR spectra of C_6D_6 in uniaxially elongated, swollen, crosslinked rubber networks. The numbers on the spectra are λ values. Samples: (a) Chloroprene rubber (sample number 4, $\phi = 0.707$); (b) butadiene-styrene copolymer (sample number 4, $\phi = 0.735$).



(b)

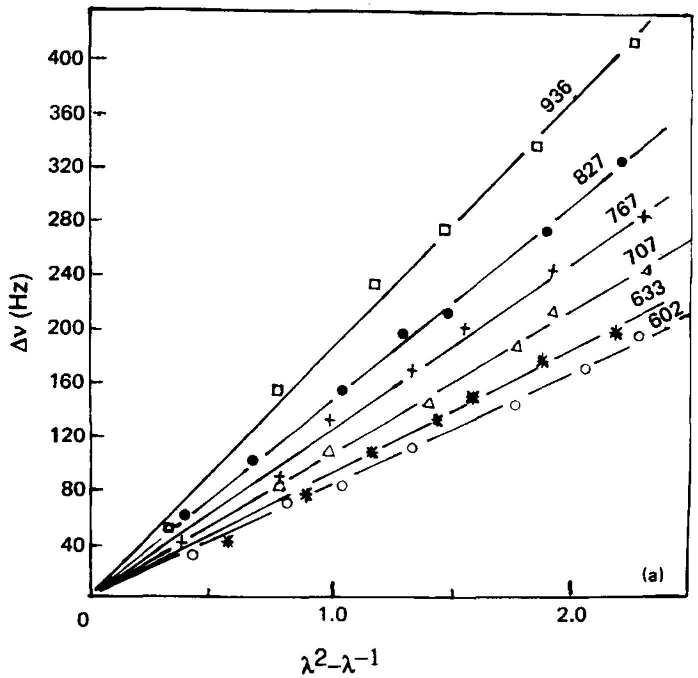
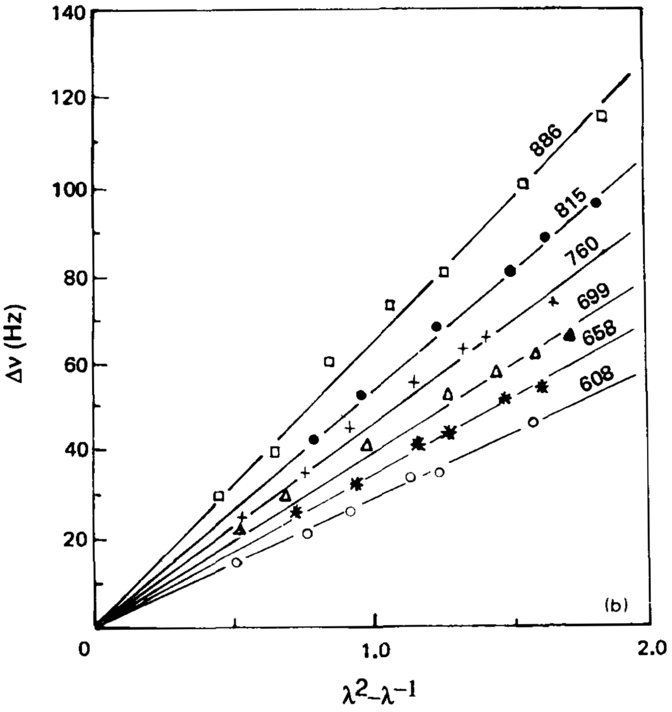


FIG. 2. Plots of $\Delta\nu$ against $\lambda^2 - \lambda^{-1}$. Numbers on the lines are ϕ values. Swelling agent: C_6D_6. Samples: (a) Chloroprene rubber (sample number 4); (b) butadiene-styrene copolymer (sample number 3).

use for various kinds of rubber. The straight lines in Fig. 3 show good agreement with Eq. (6). We can see from Table 2 that the relative number of chain segments between crosslinks calculated from Eq. (7) is comparatively close to that obtained from the Flory equation. Hence, use of f as an adjustable parameter in G is justified, and Eq. (6) is reliable.

From the experiment we find that f increases with crosslink density, i.e., G decreases with crosslink density. Moreover, linear regression analysis of f against $1/r$ shows that there is an approximately linear relation between them (see Table 3). These results are in agreement with Eq. (5). This linear relation also indicates that q' is approximately constant for the samples with different crosslink densities used in these experiments.



According to the ^{2}H NMR experimental results for chloroprene rubber and butadiene-styrene copolymer, the interaction between chain segments, which is represented by G, decreases with crosslink density. The same conclusion was obtained previously in stress-optical experiments [15].

The relation between the stress-optical coefficient C and the enhancement factor G can be expressed as follows [17]:

$$C = C^*(1 + G). \tag{9}$$

The ratios of C to C^* calculated with G values obtained by ^{2}H NMR are far

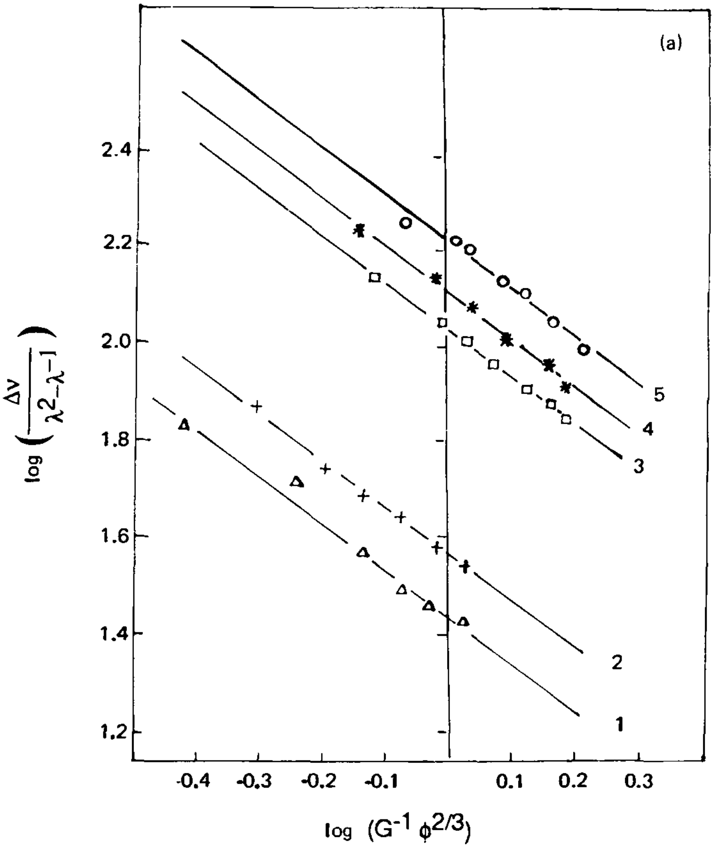


FIG. 3. Plots of log $[\Delta\nu/(\lambda^2 - \lambda^1)]$ against log $(G^{-1}\phi^{2/3})$. Numbers on the lines are the sample numbers. Samples: (a) Chloroprene rubber; (b) butadiene-styrene copolymer.

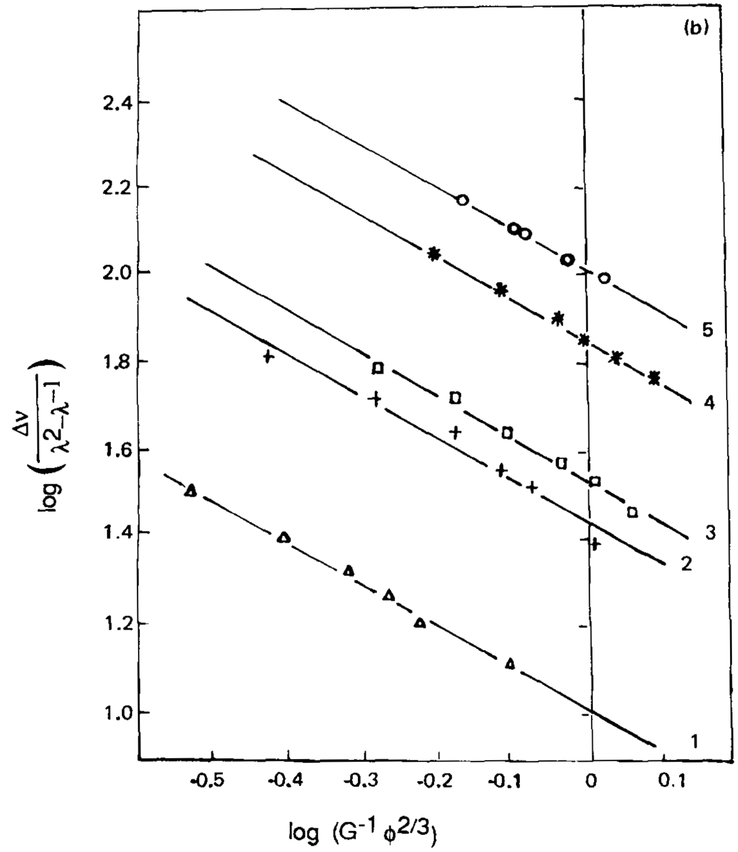

(b)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
$\log\left(\frac{\Delta v}{\lambda^2-\lambda^{-1}}\right)$
-0.5
-0.4
-0.3
-0.2
-0.1
0
0.1
$\log\,(G^{-1}\,\phi^{2/3})$
5
4
3
2
1

TABLE 2. Value of *f* and Relative Number of Monomers between Crosslinks

Polymer	Sample number	Parameter f	Ratio of N_m	
			From ^{2}H NMR	From Flory equation
Chloroprene rubber	1	0.59	6.17	5.27
	2	0.61	4.59	3.46
	3	0.76	1.53	1.40
	4	0.80	1.28	1.00
	5	0.82	1.00	1.00
Butadiene-styrene copolymer	1	0.54	10.46	13.95
	2	0.61	3.82	3.59
	4	0.66	3.04	2.11
	4	0.72	1.45	1.16
	5	0.76	1.00	1.00

TABLE 3. Linear Regression Analysis of *f* as a Function of $1/r$

Polymer	Correlation coefficient	Slope	Intercept
Chloroprene rubber	0.99	0.28	0.54
Butadiene-styrene copolymer	0.99	0.22	0.54

larger than the stress-optical experimental results although the tendency of the change of G with crosslink density is the same as that of C. The reason is that the theoretical model is too simple, and the structure of rubber is not considered. In practice, different chemical structures will produce different correlation interactions [19]. Thus, G should vary with the kind of rubber. Therefore, we may express the enhancement factor G_r of a real rubber as

$$G_r = g_k \cdot G, \qquad (10)$$

where g_k is a constant associated with the chemical structure of the rubber, which is much less than unity.

APPENDIX

Derivation of the Parameter f

The entropy of a single chain is a function of the chain end-to-end vector R and the intrachain segment vector distribution. In general, the parameter p which characterizes the extent of segment orientation is given by

$$p = \langle \cos^2 \theta \rangle = N^{-1} \sum_i N_i \cos^2 \theta_i, \tag{A1}$$

$$N = \sum_i N_i, \tag{A2}$$

where θ_i is the angle between the ith direction and the stretching direction X, and N_i is the number of segments in that direction. N is the number of links of a single chain. Here the summations extend over all the allowed directions. The X component of the chain vector x is given by

$$x = \sum_i N_i b \cos \theta_i, \tag{A3}$$

where b is the length of links.

The probability that a certain distribution $\{N_i\}$ occurs is proportional to W, given by

$$W(\{N_i\}) = N! \left(\prod_i f_i^{N_i}\right) / \left(\prod_i N_i!\right), \tag{A4}$$

where f_i is the *a priori* probability that the segment lies in the ith direction. The distribution $N_i°$ is obtained by maximizing Eq. (A4) by the Lagrange method when p and x are fixed:

$$N_i^\circ = f_i \exp(\lambda) \exp(\mu b \cos \theta_i) \exp(\beta \cos^2 \theta_i). \tag{A5}$$

The values of λ, β, and μ can be determined by Eqs. (A1), (A2), and (A3) under the condition of N_i°. We can obtain the entropy of a single chain s by using Eqs. (A1)–(A5):

$$s = k \ln W(\{N_i{}^\circ\}) = k(N \ln N - \lambda N - \mu bx - \beta pN). \tag{A6}$$

Differentiating Eq. (A6) with respect to p with fixed x, we have

$$(\partial s/\partial p)_x = -k\beta N. \tag{A7}$$

(I) Entropy of the Freely Jointed Chain

For this walk model, θ is continuous and f_i is proportional to $\sin \theta_i$ in a polar coordinate system. Inserting $N_i{}^\circ$ in Eqs. (A1)-(A3), respectively, and setting $t = \cos \theta$, we have

$$N = [\exp(\lambda)/2]\int_{-1}^{1} \exp(\mu bt) \exp(\beta t^2)\, dt, \tag{A8}$$

$$p = [\int_{-1}^{1} t^2 \exp(\mu bt) \exp(\beta t^2) dt]/[\int_{-1}^{1} \exp(\mu bt) \exp(\beta t^2) dt], \tag{A9}$$

$$x/Nb = [\int_{-1}^{1} t \exp(\mu bt) \exp(\beta t^2)\, dt]/ [\int_{-1}^{1} \exp(\mu bt) \exp(\beta t^2)\, dt]. \tag{A10}$$

Expanding Eqs. (A9) and (A10) around $\mu = \beta = 0$, retaining μb and β as well as the results of the integration to the second-order small term, we obtain

$$\beta \doteq [45/4 + 27(x/Nb)^2](p - 1/3) - (9/2)(x/Nb)^2. \tag{A11}$$

$(x/Nb)^2$ cannot be ignored when N is not very large.

When there is no restriction on p; which corresponds to setting $\beta = 0$, we can obtain p^* from Eq. (A9):

$$p^* \doteq 1/3 + (2/5)(x/Nb)^2. \tag{A12}$$

Inserting Eq. (A11) in Eq. (A7) and integrating it with respect to p from p^* to p ($\beta = 0$ to β), we have, with the aid of Eq. (A12), the entropy s, given by

$$s/kN = -[45/8 + (27/2)(x/Nb)^2]q^2 + c(x)/kN, \tag{A13}$$

$$q = p - p^*, \tag{A14}$$

where $c(x)$, a function only of x, can be identified with s^*. From this, the following relation is derived:

$$\Delta s = s - s^* = -[45/8 + (27/2)(x/Nb)]kNq^2. \tag{A15}$$

(II) Entropy of the Random-Lattice-Walk Chain

For this model, $i = \pm X, \pm Y, \pm Z, f_i = 1/6$, replacing the integrals in Eqs. (A8)-(A10) by summations, we can obtain the restricted equation of the parameter of this model:

$$N = [\exp(\lambda)/6][\exp(\beta)\exp(\mu b) + \exp(\beta)\exp(-\mu b) + 4], \tag{A16}$$

$$p = \exp(\beta)[\exp(\mu b) + \exp(-\mu b)]/[\exp(\beta)\exp(\mu b) + \exp(\beta)\exp(-\mu b) + 4], \tag{A17}$$

$$x/Nb = \exp(\beta)[\exp(\mu b) - \exp(-\mu b)]/[\exp(\beta)\exp(\mu b) + \exp(\beta)\exp(-\mu b) + 4]. \tag{A18}$$

Expanding eqs. (A17) and (A18) and retaining β and μb as well as the results of the integration to the second-order small term, we have

$$\beta \doteq [9/2 + 27(x/Nb)^2](p - 1/3) - (9/2)(x/Nb)^2. \tag{A19}$$

On setting $\beta = 0$, p^* is obtained from Eq. (A17) as follows:

$$p^* = 1/3 + (x/Nb)^2. \tag{A20}$$

From Eq. (A7) we have

$$s/kN = -[9/4 + (27/2)(x/Nb)^2]q^2 + c(x)/kN. \tag{A21}$$

Therefore,

$$\Delta s = -[9/4 + (27/2)(x/Nb)^2]kNq^2. \tag{A22}$$

Summarizing the above two models, we can cast the results in the following general form:

$$\Delta s = -f'kNq^2, \tag{A23}$$

$$f' = f_0' + a'(x/Nb)^2. \tag{A24}$$

For our freely jointed chain model,

$$f_0' = 45/8, \qquad a' = 27/2,$$

and for our random walk model,

$$f' = 9/4, \qquad a' = 27/2.$$

Due to symmetry, the average values of the Y and Z components are zero. Therefore, the average r vector is uniform with the X-axis. For a random link with $\bar{R}^2 = N^2b$, f' can be written as

$$f' = f_0' + a'/N. \tag{A25}$$

Equation (A23) is valid only when q is small and $|R|$ is small compared to the contour length of the chain. In other words, the entropy change Δs due to changing the segment distribution by a small amount q is independent of the chain vector (and hence of p^*), at least for small deformations.

In this case, the entropy change ΔS of the network system due to changing the overall distribution by a small amount $\bar{q} = \bar{p} - \bar{p}^*$ is obviously independent of the chain vector distribution. It can be shown that, when Δs is given by Eq. (A23), ΔS may be given as the sum of the entropy changes of the individual chains with a uniform change $\bar{q}$, i.e.,

$$\Delta S(\bar{q}) = M\Delta s(\bar{q}) = -kf'NM\bar{q}^2, \tag{A26}$$

where M is the number of chains. From $S(\bar{q})$, the expression for G can be derived [17] (Eq. A3 in this paper); in it,

$$f = (4/9)f'. \tag{A27}$$

CONCLUSIONS

It has been found that the orientational order due to the interaction between chain segments increases, but the relative enhancement of this order, which is expressed by G, decreases with increasing crosslink density. The formula relating the parameter f in G with the number of chain segments between crosslinks has been derived. The relative number of chain segments (monomers) between crosslinks has been estimated. We conjecture that the enhancement factor G_r of real rubber depends on the kind of rubber. According to the ^{2}H NMR results, the interaction between chain segments decreases with increasing crosslink density. The same conclusion was obtained previously by a stress-optical study [15].

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