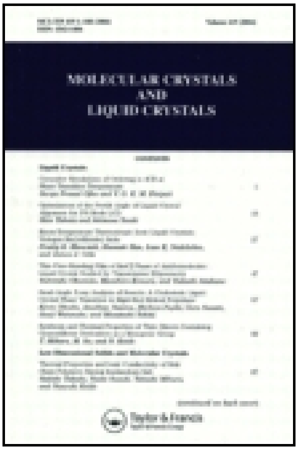

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# Probing Orientation Phenomena in Strained Rubbers with Deuterium Nuclear Magnetic Resonance

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# PROBING ORIENTATION PHENOMENA IN STRAINED RUBBERS WITH DEUTERIUM NUCLEAR MAGNETIC RESONANCE

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The orientational order generated in rubbers by uniaxial stress is probed with deuterium NMR. Deuterated swelling agents or labelled polymeric chain segments exhibit a residual quadrupolar interaction when the elastomer is under constraint. This induced anisotropy has a distinctive dependence on the network extension ratio and the cross-linking density of the material.

## 1. INTRODUCTION

The rubber state exists in variety of flexible macromolecular chains (polyisoprenes, polybutadienes) which are held in a threedimensional array by chemical crosslinks (covalent bonds) and physical junctions(entanglements). This state is unique in that the constituent polymer chains are fluid but the bulk material does not flow and so retains its form.

The rubber may be deformed elastically by external forces eg uniaxial tension; optical birefringence measurerements show that the system becomes anisotropic. How does the macroscopic strain affect the chain behaviour? Such a question, related to the deformation involved at the molecular level, has given rise to controversial discussions. This is the reason why various microscopic techniques (neutron scattering, fluorescent polarization) are currently being used to examine elastomeric chains under deformation. Among the techniques sensitive to the orientational behaviour we propose to use the nuclear magnetic resonance and we know from studies on various systems of deuterated liquid crystals that the deuterium magnetic resonance ($^2$H-NMR) is well adapted for probing local ordering. Specifically, here we use this technique to study the orientational order generated in uniaxially deformed rubbers. The measurements are done either on deuterated swelling agents, as NMR probes, or directly on labelled polymeric chains; clearly these experiments allow the detection of an orientational anisotropy at the chain level and give access to the corresponding order parameter; systematics studies show that this order has an explicit dependence on the network extension ratio and the cross-linking density.

## 2. BACKGROUND

### 2.1. Rubber Elasticity

The classic description of rubber elasticity is based on a single-gaussian-chain model [1]. Under the assumption of constant volume and affine molecular deformation such a theory leads to a relation between the stress $\sigma$(referred to the strained cross section) and the extension ratio $\lambda(\lambda = L/L_o$ where L and $L_o$ are the strained and unstrained lengths of the elastomer). For an uniaxial tension and in the limit of low deformation, the stress-strain relation is

$$\sigma \propto n\, k_B T\, (\lambda^2 - \lambda^{-1}) \qquad (1)$$

where n and T are the number of chains per unit volume and the temperature respectively[1].

The hypothesis of molecular affine deformation determines the orientational distribution of the chain segments relative to the chain end-to-end vectors $\vec{R}$ relative to the direction of the applied constraint. Then, from the orientational distribution of the chain segments relative to $\vec{R}$ one can. obtain the second moment $<P_2>$ of the segmental orientation function relative to the constraint axis[2]:

$$<P_2> \propto \frac{1}{N}\,(\lambda^2 - \lambda^{-1}) + 0\,(\frac{\lambda^4}{N^2}) \qquad (2)$$

N is the number of statistical segments per chain. In the limit of low deformation, $<P_2>$ and $\sigma$ have the same $\lambda$-dependence.

### 2.2. Deuterium NMR

The general features of $^2$H-NMR in anisotropic fluids have been discussed in detail in reference 3 . Briefly, we recall that if rapid molecular uniaxial reorientations take place, the observed quadrupolar interaction is no longer averaged. The effect of this residual coupling is to split the NMR line into a doublet whose spacing $\Delta\nu$ may be written in frequency units as:

$$\Delta\nu \propto \nu_Q\; P_2(\cos\Omega)\; <P_2(\cos\theta(t))> \qquad (3)$$

where $\nu_Q$ designates the static quadrupolar coupling $\Omega$ and $\theta$ are the angles between the direction of the macroscopic symmetry axis (ie this one of the applied tension in our case) with the static magnetic field $B_o$ and the C-D bond respectively. Then the effective quadrupolar coupling constant is $\nu_Q \langle P_2(\cos\theta(t))\rangle$ where the average can be defined as the so-called orientational order parameter of the C-D bond relative to the symmetry axis under interest.

The current resolution available for observing $\Delta\nu$ ($\sim$ 1 HZ) in conjunction with the inherently large value of the C-D quadrupolar constants $\nu_Q$ ($\sim$ 200 KHz) enables one to measure orientational order differing from the isotropic state by as little as a few parts in $10^5$.

## 3. EXPERIMENTAL

### 3.1. Deuterium NMR approach

From the experimental point of view, the $^2$H-NMR may be conveniently done either on deuterated swelling agents [4], used as NMR probes of the polymeric matrix, or directly on labelled polymeric chains [5]. We recall that the probe method has been extensively used in the liquid crystal field to investigate various systems [6].

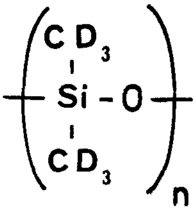
All $^2$H-NMR spectra were obtained after signal averaging from FT NMR equipment operating with a conventional electromagnet (the magnetic field $\vec{B}_o$ is perpendicular to the stretching direction, $\Omega$= 90°) or a superconducting magnet ($\vec{B}_o$ is parallel to the stretching direction, $\Omega$=0°).

### 3.2. Materials

Most experiments were performed on hexadeuteriobenzene dissolved in diene rubbers and on labelled chains of some silicone rubbers.

The set of diene rubbers are tetrafunctional polybutadiene (PB) networks; all these networks were prepared from peroxide cross-linking of a polybutadiene precursor (Diene 45 NF). The cross-linking reaction was always carried out in the dry state varying the curing agent concentration from 0.1% to 1,2%. Each network is characterized by its mean molecular weight $M_c$ derived from the corresponding values of the volume fraction of polymer $\Phi_e$ at swelling equilibrium [7], using cyclohexane as a good solvent.

The set of silicone rubbers are end-linked polydimethyl siloxane model networks, containing a known fraction (∿20%) of perdeuterated chains PDMS(D).

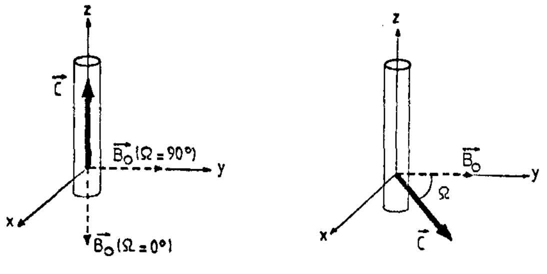


$$\left( \overset{CD_3}{\underset{CD_3}{Si}} - O \right)_n$$

These networks were synthetized by reacting stoichiometric mixtures of labelled and unlabelled precursors chains with tetrafunctional cross-linkers [8]; the end-linking reaction was carried out in toluene of 70% polymer concentration. The synthesis of perdeuterated precursors is described in reference 9. For the present investigation, four model networks has been used; they are characterized by the molecular weight between cross-links $M_n$ ie.the molecular weight of the precursor ($3.000 < M_n < 25.000 g.mol.^{-1}$)

### 3.3. Uniaxial stress

Tension was applied to samples the nominal dimensions of which were typically 40 mm x 6 mm x 1 mm as described in reference [4] so that the stretching direction is coincident



a) tension

b) compression

FIGURE 1 Orientation of the spectrometer magnetic field $B_o$ with respect to the applied uniaxial stress C: a) $B_o$ is perpendicular or parallel to the direction of the elongation, coincident with the NMR tube axis; b) $B_o$ is always along the y axis while the direction of the compression may be varied within the plane (x y) by rotating the NMR tube around its vertical axis.

with the axis of the NMR tube, i.e. parallel or at right angles to the spectrometer magnetic field $\vec{B}_o$. The extension ratio $\lambda = \frac{L}{L_o}$ was estimated from the stretched and unstretched lengths measured between marks on the sample; L was determined to within ± 0,2 mm.

The compression was obtained by squeezing a small piece of the sample between two semi-cylindrical jaws. This assembly was introduced into the bottom of the NMR tube; in this way the angle Ω between the compression direction relative to $\vec{B}_o$ can be varied continuously, rotating the tube by hand around its vertical axis, as indicated on figure 1. The compression ratio ($\lambda < 1$) was estimated roughly from the thickness of the sample.

Deuterated probes ($C_6D_6$) were dissolved in the elastomer by exposing dry (preweighed) samples to the vapor/liquid of the swelling agents. The volume fraction of polymer $\phi$ was determined by weighing the samples before and after the NMR experiment. For instance each sample of the series of PB has been studied at a polymer volume fraction $\phi$ equal to 0,9 and it has been checked that this degree of swelling does not significantly evolve during any one experiment.

## 4. RESULTS

Figure 2 shows the change of the $^2$H-NMR spectrum of deuterobenzene in a PB network as the sample is uniaxially elongated. The spectrum changes from a single narrow line in the relaxed state ($\lambda$ = 1) to quadrupolar doublets. The observed residual interaction for $\lambda$ >1 are indicative of anisotropic reorientational diffusion for $C_6D_6$ constrained by the uniaxial field generated by the elongated network chains. The corresponding orientational order parameter $<P_2>$ of the benzene $C_6$ axis can be deduced from the relation (3) with $\nu_Q$ = 190 kHZ : typically $<P_2> = 2.5.10^{-3}$ for a relative elongation of 30%. This strained induced

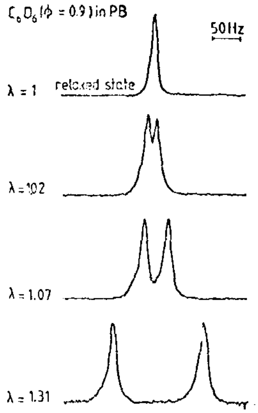


FIGURE 2 13 MHZ $^2$H-NMR spectra of $C_6D_6$ in a uniaxially strained PB network (polymer volume fraction $\phi$ = 0,9).

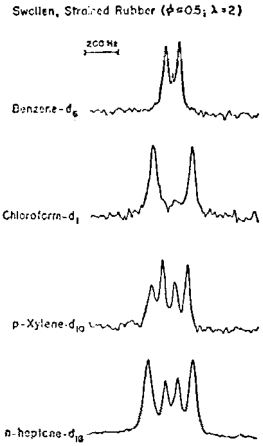


FIGURE 3 $^2$H-NMR spectra of various deuterated swelling agents in a polyisoprene network ($M_c$ ∿3500). The latter two solvents have chemically inequivalent deuterons and so exhibit more than one quadrupolar doublet.

orientation appears quite general, regardless of the nature of the polymer matrix and of the probe molecule. For instance the figure 3 demonstrates that nearly spherical swelling agents ($CDC_{13}$) as well as completely flexible swelling agents (n-heptane-$D_{16}$) are also oriented in the deformed network.

Figure 4 shows characteristic specta of PDMS(D) as the sample is uniaxially compressed ($\lambda < 1$) or elongated ($\lambda > 1$) along a direction perpendicular to the steady magnetic field $B_o$( $\Omega = 90°$): here too quadrupolar doublets ($\Delta\nu \neq 0$) are still observed for $\lambda \neq 1$ but in part due to a broader linewidth in the relaxed state ($\delta\nu \sim 40$ HZ), the observed resolution is lower than in the experiments on dissolved probes. The complete angular variation $\Delta\nu(\Omega)$ reported in figure 5 shows that it reproduces exactly $|P_2(\cos\Omega)|$ as in

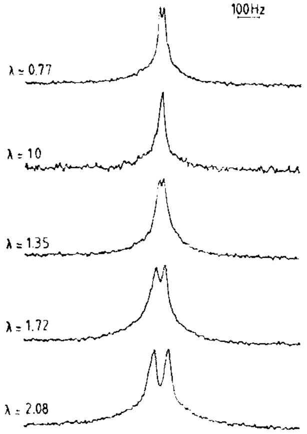


FIGURE 4 13 MHZ $^2$H-NMR spectra of perdeuterated chains of PDMS network as the sample is uniaxially compressed ($\lambda<1$) or elongated ($\lambda > 1$).

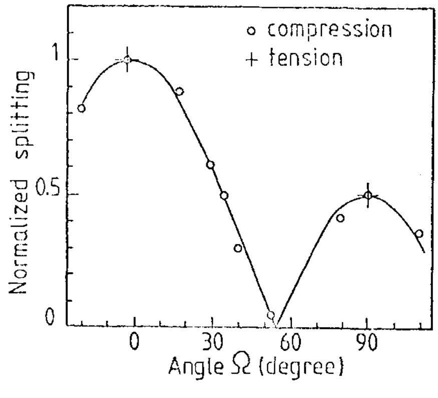


FIGURE 5 Variation of the normalized splittings of the PDMS(D) as a function of the angle between the uniaxial constraint and the steady magnetic field. The continuous line is the function $|P_2\ (\cos\Omega)|$.

as in relation (3). So clearly the polymer chain (or portions of them) which give rise to the doublet may be visualized as a uniaxial fluid of segments exhibiting anisotropic reorientational diffusion with respect to the direction of the applied constraint. For instance we may consider that the chain segments diffuse in such a way that they cannot be oriented in any other direction than along the axis of stress for times longer than a few $10^{-5}$ sec.

What is the relationship between the order parameters $P_2$ measured on the solvent probes and on the chain segments? Due to the overlap of spectra, the answer to this question required successive comparisons of the following systems: PDMS(D) swollen with some $C_6H_6$ and PDMS (H) swollen with $C_6D_6$. Under the same degree of swelling ($\phi$ = 0,9) and for the same cross-linking density of PDMS networks (Mn = 25.000) we find that the respective $<P_2>$ remain proportional when $\lambda$ varies and differ by less than one order of magnitude: for $\lambda$ = 1,4 the order parameter of the Si-$CD_3$ bonds is equal to $8.10^{-4}$ while this one of the symmetry axis of the benzene is equal to $3.10^{-4}$. This result shows that, for such degree of swelling, the solvent molecules are faithful probes of the polymeric environment.

## 5. DEPENDENCE ON λ AND N.

Figure 6 illustrates the variation of the quadrupolar splittings $\Delta\nu$ with the elongation for various cross-linking density in PB samples[10]. It appears that the data fit well fit with a $\lambda^2 - \lambda^{-1}$ law; the same $\lambda$- dependence is also obtained via the direct investigation of PDMS(D) compounds as shown on Figure 7. These results versus $\lambda$, related to the isovolume character of the orientation process, is in

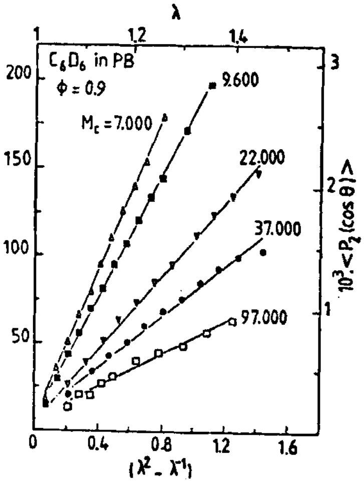


FIGURE 6 Splittings $\Delta\nu$ and calculated order parameter $\langle P_2\rangle$ of $C_6D_6$ in PB networks vs $\lambda^2 - \lambda^{-1}$ for various cross-linking densities at constant polymer volume fraction $\phi$. For reason of clarity all the samples studied have not been reported in this figure.

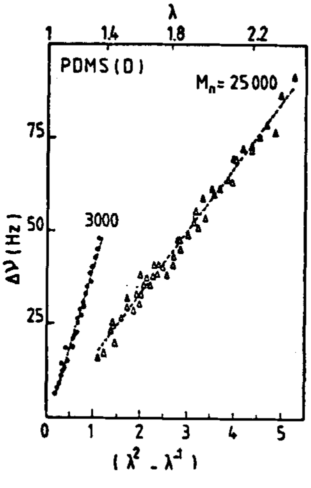


FIGURE 7 Splittings $\Delta\nu$ of the labelled silicone rubbers networks VS $\lambda^2 - \lambda^{-1}$. For reason of clarity data of two samples only are reported.

agreement with the relation (2) in the low deformation limit ($\lambda^2/N \ll 1$).

The other stricking feature of the observed averaging process is that the magnitude of the splitting $\Delta\nu$ increases with the cross-linking density for a given elongation $\lambda$ . This result is in qualitative agreement with the classical description of the phenomenon; indeed, according to the relation (2) above, the induced order has to decrease with the polymer mass between chemical jonctions. However, for both types of elastomers studied, the variation of the slope is lower than one calculated from the expression (2): for instance the ratio between the extreme value of p is 5 in the case of PB while the corresponding ratio of the mass $M_c$ is 14; in the case of PDMS a ratio of 3 has to be compared with 8.

Regarding this departure from the classical $N^{-1}$ variation in the expression (2), the experiments on PDMS may appear particularly relevant because they were carried out on well defined end-linked networks by observing the polymer chain directly. But even in this case, it may always be argued that the number of chain segments does not take into account the presence of trapped entanglements so that the molecular weight $M_n$ between adjacent junctions does not correctly define the network structure under interest. This point shows how difficult it is to know the mesh size which plays a role in our investigation. Under these conditions a better understanding of the experiments requires to relate the measured order parameter to the thermodynamic properties of the network rather than to a geometrical parameter which is always somewhat ill-defined for any non-ideal system. So we choose to analyse our data versus a <u>macroscopic</u>

variable, sensitive to the topological structure of the network[10]. For instance such a variable may be the elastic modulus G or the swelling equilibrium volume fraction of the polymer $\Phi_e$; indeed both of these characteristics of the network are sensitive to chemical and physical junctions.

As shown in Figure 8 the induced orientational order is related to the network structure in the same way as the equilibrium degree of swelling $\Phi_e$: for the two kinds of investigated rubbers the various slopes vary linearly with $\Phi_e$; in addition, each extrapolated straight line goes through the origin; this corresponds to the fact that in the melt ( $\Phi_e = 0$) no permanent orientation can be generated ($\Delta\nu = 0$). It might be argued here that the observed linear dependence is specific to the solvent used for the

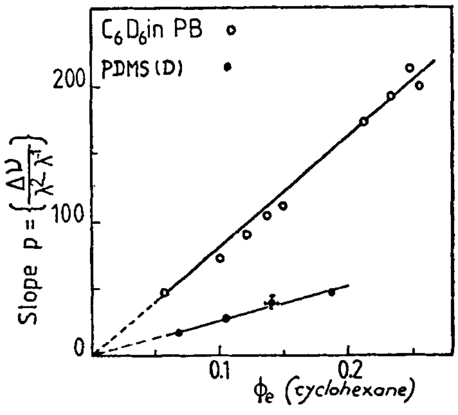


FIGURE 8 Slopes p of $\Delta\nu$ VS $\lambda^2-\lambda^{-1}$ data of figures 6 and 7 against the swelling equilibrium fraction of polymer $\Phi_e$ in cyclohexane for the PB and PDMS(D) networks respectively.

determination of $\Phi_e$; in fact, according to the experimental results of S.Candau et al [11], another good solvent would not affect the linearity $\Delta\nu(\Phi_e)$ but would only modify the slope.

## 6. CONCLUDING REMARKS

This work on strained fluid elastomers, which has been somewhat inspired by previous studies on liquid crystals, show that the $^2$H-NMR is a powerful tool for probing polymeric chain ordering. Moreover the fact that the investigation on dissolved probes led to the same result as the direct study on the polymeric backbone does suggest that the reorientational diffusion of the swelling agents is strongly coupled to the segment ordering of the polymer. Such a coupling certainly involves orientational correlations within the deformed network. In any case the present work emphasizes the reliability of the solvent-probe method for testing orientational phenomena in strained rubbers.

According to this study the orientational order generated in strained rubbers is simply proportional to the equilibrium swelling degree $\Phi_e$ when the cross-linking density is changed. From this phenomenological relationship, established on two sets of samples, $\Phi_e$ appears as a macroscopic variable well-adapted to characterizing the topological structure of the network in regard to the induced anisotropy.

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