

## Proton magnetic relaxation observation of weak gel stretching

### Evidence for affine deformation

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#### SUMMARY

Uniaxially elongated crosslinked polybutadiene networks were observed from the transverse magnetization of protons attached to polymer chains. The residual energy of dipole-dipole interactions characterizing the relaxation function was shown to vary as a linear function of the expression  $\lambda^2 - \lambda^{-1}$ ; the stretching ratio  $\lambda$  was varied from 1 to 3. This result gives evidence for affine deformation of crosslinks. The orientational order of monomeric units perceived from NMR proved more sensitive to variations of crosslinking concentrations and/or chain molecular weights than corresponding elastic moduli.

#### I - INTRODUCTION

It is now currently considered that macroscopic gel properties result from the collective behaviour of statistical structural units. These must be defined in a suitable way and their exact determination is one of the main problems encountered in the description of gel systems. The average size of these statistical domains is supposed to calibrate the pertinent semi-local space-scale of description of gel swelling processes or of mechanical gel properties. It is known that even in the case where gels are synthesized from end-linked calibrated chains, the gel structural unit is not defined in a simple way because of the existence of entanglements. More precisely, it has been experimentally shown that both the maximum swelling at equilibrium with a liquid and the elastic modulus closely depend upon the polymer concentration prepared prior to the gelation process (1). Whenever it can be considered that structural units are determined in a satisfactory way by applying a pure topological analysis to the gel system, another problem still arises from the difficulty to exactly describe and then to evaluate effects induced by monomer unit-monomer unit interactions on the one hand and by neighbouring crosslinks, on the other hand.

In this respect, NMR has proved a convenient tool to investigate hindrance effects affecting stochastic motions of monomeric units. More precisely, NMR is sensitive to all hindrance effects which manifest as deviations of monomeric unit motions from isotropic rotational diffusion processes. This diffusional asymmetry property induces a non-zero average of spin-spin tensorial interactions. The resulting residual energy  $\bar{H}_d$  is conveniently measured from the transverse magnetic relaxation function  $M_x(\Delta t)$  of protons or  $^{13}\text{C}$  nuclei. Transient effects of diffusional processes can be actually ignored. The main hindrance effect undergone by monomeric units is induced by topological constraints acting on chain segments. Most polymer systems can be pictured from an ensemble of elementary chain segments of fixed end-

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points determined from entanglements in a melt or from crosslinks in a gel. Whereas the non-isotropic character of diffusional motions of monomeric units is permanent in a gel, it is only temporary in a melt; in this last case, the non-zero average of spin-spin interactions  $\bar{n}\Delta_e$  is perceived as a time independent quantity whenever the life-time of entanglements is longer than  $\Delta_e^{-1}$ .

Considering a weakly stretched chain segment, the residual energy of dipole-dipole interactions within non-interacting proton pairs attached to skeletal bonds can be expressed as a simple function :

$$\bar{n} \epsilon_e \propto \bar{n} \Delta_G \langle \vec{r}_e \rangle^2 / L_e^2 \quad (1)$$

where  $\langle \vec{r}_e \rangle$  is the fixed end-separation vector of the chain segment and  $L_e$  is the chain length;  $\bar{n} \Delta_G$  is the dipole-dipole interaction observed in the glassy state (2).

Formula (1) has been already applied to the investigation of swelling properties of calibrated polydimethylsiloxane gels (3). The progressive unfolding of elementary chains has been shown to be accompanied by a residual energy variation obeying the formula :

$$\bar{n} \Delta_e \propto \bar{n} \Delta_G Q^{2/3} v_c^{2/3} \quad (2)$$

where  $Q$  is the gel swelling ratio while  $v_c$  is the initial concentration of gelation. Formula (2) relies upon two features :

i) elementary chain segments i.e. structural domains of the gel are determined by trapped entanglements; their average chain length is given by  $L_e \propto v_c^{-1/4}$ ;

ii) elementary chain segments obey a packing condition :  $Q \propto \langle r_e \rangle^3 / L_e$ .

It must be noted that the asymmetry property easily perceived from quantum coherence properties of the transverse nuclear magnetization includes all hindrance effects whatever detailed transient mechanisms inducing them. More precisely, it is worth emphasizing that a number of studies have shown that both spin-lattice relaxation rates  $T_1^{-1}$  and  $T_1^{-1}$  carrying out in the rotating coordinate frame are not significantly affected by changes in overall chain length and in the crosslink density in a gel. For example, it has been shown that the range of crosslink density in cis-1,4-polybutadiene must be explored down to about ten repeat units to observe small variations of both  $T_1^{-1}$  and  $T_1^{-1}$  rates (4).

NMR may also provide information about properties of a stretched gel by observing relaxation and diffusion of penetrants. For example, properties of a crosslinked natural cis-polyisoprene was investigated by using hexafluorobenzene and n-hexadecane as penetrants. The transverse magnetic relaxation function of protons was shown to be anisotropic and elongation dependent whereas solvent diffusion rates were found to be isotropic and elongation independent (5). Then, a similar approach was proposed by observing deuterium magnetic resonance of penetrants like benzene. The quadrupolar resonance spectrum of deuterium nuclei exhibits a typical doublet (6, 7). Its splitting is a function of the stretching ratio  $\lambda$ , through the difference  $\beta = \lambda^2 - \lambda^{-1}$ . Deuterated polydimethylsiloxane gels also present a resonance doublet, with a similar splitting variation. In both cases, the  $\lambda$  dependence reveals an affine deformation of the gels. Although the interaction of penetrants with monomeric units is not clearly defined, yet, it can be considered that solvent molecules reflect directional properties of chain segments, induced by gel stretching.

The purpose of the present work is to show that semi-local properties of stretched gels can be conveniently investigated from the transverse magnetic relaxation of protons attached to polybutadiene chains.

## II. EXPERIMENTAL

### II.a - Materials

The materials used in this study were crosslinked polybutadiene networks supplied by the Manufacture Française des Pneumatiques Michelin. Sample references are listed in Table 1. The approximate composition was 42% cis 1-4, 50% trans 1-4 and 8% 1,2 (by weight). The crosslinking reaction was carried out with a sulphur cure at two concentrations : 0.5% or 1%. Molecular weights were determined from Gel Permeation Chromatography (GPC). For each of these materials, measurements of the elastic modulus G were performed from stress-strain data corresponding to a low uniaxial elongation ; the temperature was 298K.

Table 1 - Characterization of the three samples studied

Sample	Mw g/mole	Mn g/mole	Crosslink agent (Sulphur) %	G (MPa)
A	267,000	250,000	1.0	0.68
B	267,000	250,000	0.5	0.42
C	428,000	363,000	0.5	0.63

### II.b - $^1\text{H}$ NMR

NMR experiments were performed using a CXP 100 Bruker spectrometer operating at a  $^1\text{H}$  frequency of 60 MHz. The magnetic field is normal to the stretching direction. All relaxation functions were measured by Carr Purcell spin echoes experiments and by pseudo-solid echoes. The pseudo-solid echoes have been described elsewhere (8). They are formed from the following pulse-sequence :

$$\left( \frac{\pi}{2}/y \right) - \frac{\tau}{2} - (\pi/y) - \frac{\tau}{2} - \left( \frac{\pi}{2}/-x \right) - \left[ \frac{\tau_1}{2} - (\pi/y) - \frac{\tau_1}{2} - \frac{\tau_1}{2} - (\pi/y) - \frac{\tau_1}{2} - \frac{\tau_1}{2} - (\pi/-y) - \frac{\tau_1}{2} - \frac{\tau_1}{2} - (\pi/y) - \frac{\tau_1}{2} - \right]_N$$

### II.c - Stretching probe

Polybutadiene rubbers were supplied in sheets of 0.9 mm thickness. They were cut into rectangular strips (about 5 x 4 mm). The two extremities of each strip were firmly stuck with a cyanoacrylate instant adhesive on two pieces of glass. The upper one was connected to a teflon rod whereas the lower one was fixed. All the device was fitted into a 10 mm diameter tube. A micrometric calibrated Knurled screw operates the displacement of the teflon rod allowing uniaxial extension of the sample parallel to the tube axis. The lengths of the sample after and before stretching, L and  $L_0$ , were determined within a precision of  $\pm 0.05$  mm. The extension ratio  $\lambda = L/L_0$  was derived with a precision of 2%.

## III. EVIDENCE FOR A RESIDUAL ENERGY OF PROTON-PROTON INTERACTIONS

Before describing properties of elongated gels as they are perceived from NMR, it is necessary to prove that a residual energy  $\hbar\Delta_e$  of spin-spin in-

interactions does exist within unstretched samples. This residual energy may entirely govern the spin-spin relaxation process. It thus induces a solid behaviour of the transverse magnetic relaxation function perceived by forming spin-echoes which were called pseudo-solid echoes because they do not result from the presence of static dipole-dipole interactions (9). It has been recently shown that the pseudo-solid echoes obey specific properties when they result from a pure residual energy of spin-spin interactions. In this use, for example, the slope

$$\left. \frac{\partial M_x^e(t, \tau)}{\partial t} \right|_{t=\tau_+}$$

of the time function describing the echo formed from a time  $\tau_+$ , must be opposite of the slope

$$\left. \frac{d M_x(\Delta_e t)}{d t} \right|_{t=\tau_-}$$

, measured from the relaxation function  $M_x(\Delta_e t)$  at the time  $\tau_-$ . However, it is more convenient to observe another specific property characterizing the function  $M_x^e(t, \tau)$  drawn by varying the time interval  $\tau$  and by keeping a fixed time  $t$ . It may be asserted that the spin-spin relaxation process is not entirely governed by a pure residual energy  $\bar{\Delta}_e$  and that time fluctuations are also involved in the relaxation function, unless the function  $M_x^e(t, \tau)$  obeys a pure symmetry property with respect to  $\tau = t/2$ .

### III.a - Unstretched gel

Pseudo-solid echoes observed in sample B are shown in Fig. 1a. Several functions  $M_x^e(t, \tau)$  derived from Fig. 1a were drawn in Fig. 1b ; they correspond to different values of the fixed time  $t$ . From a glance at both figures, it is clearly seen that pseudo-solid spin-echoes reflect the existence of a pure residual energy distributed along the whole relaxation function  $M_x(\Delta_e t)$ .

### III.b - Stretched gel

Pseudo-solid spin-echoes were also formed from the same sample B, uniaxially elongated in the NMR probe ; they are illustrated by Fig. 2a ;  $M_x^e(t, \tau)$  functions derived from this figure are sharper than those drawn from the unstretched sample (Fig. 2b). This result indicates a residual energy enhancement effect induced by gel elongation.

### III.c - Evidence for chain elongation in unstretched gels

Taking formula (1) into consideration, the main feature perceived from the observation of a residual energy reported in section III.a concerns a slight elongation of chains, even in the absence of any gel stretching. The distribution of orientations of elongation directions is of course isotropic. This stretching effect is clearly assigned to the presence of topological constraints whether they are represented by crosslinks or by trapped entanglements. This NMR result is entirely compatible with the phantom network model proposed to describe swelling properties as well as elongation ones (10). Consecutive crosslinks or entanglements determine chain segments which are characterized by non-zero average end-separation vectors ;  $\langle \vec{r}_e \rangle \neq 0$  for any chain segment. Chain junctions may however fluctuate around mean positions in space. The observation of a residual spin-spin

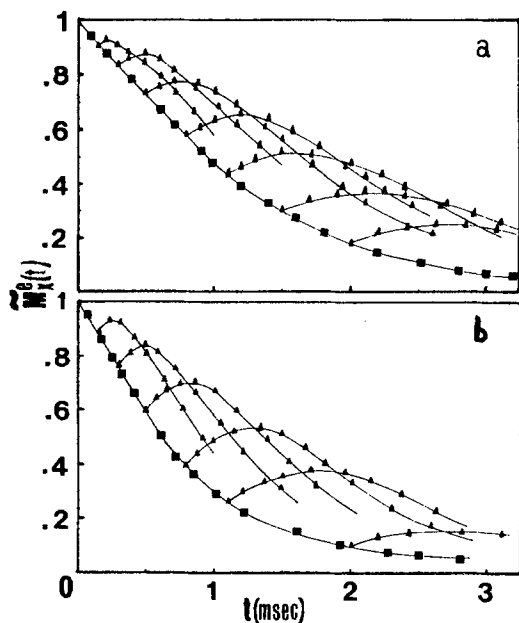


Fig. 1 - Transverse magnetic functions (■) and pseudo-solid spin-echoes (▲) obtained for several times  $\tau$  observed from sample B.

- a) undeformed state ( $\lambda = 1$ )  
 b) stretched state ( $\lambda = 2.50$ )

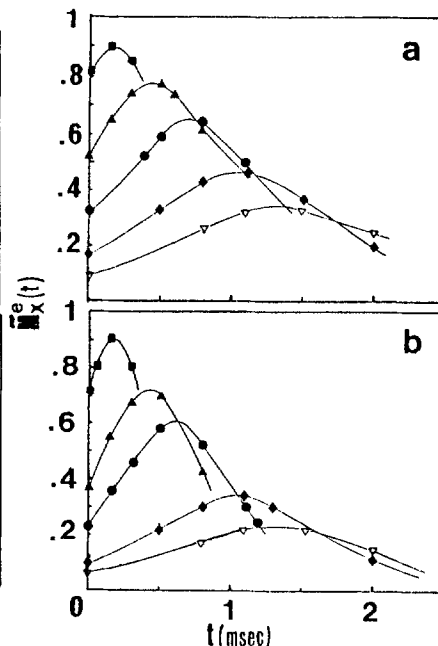


Fig. 2 - Spin-echoes functions  $M_x(t)$  observed at a given time  $t$  were represented as a function of the spin echo origin  $\tau < t$ .

- a) undeformed state ( $\lambda = 1$ ) ;  
 (■ :  $t = 0.35$  msec, ▲ :  $t = 0.90$  msec, ● :  $t = 1.40$  msec, ◆ :  $t = 2.10$  msec, ▽ :  $t = 2.65$  msec) ;  
 b) stretched state ( $\lambda = 2.5$ ) ;  
 (■ :  $t = 0.35$  msec, ▲ :  $t = 0.85$  msec, ● :  $t = 1.20$  msec, ◆ :  $t = 2.10$  msec, ▽ :  $t = 2.60$  msec).

energy in unstretched gels is contrasted to the absence of splitting of the resonance spectrum of deuterated penetrants or deuterated chains. The origin of this zero splitting effect is still unexplained (11).

#### IV. ELONGATION EFFECT

Samples A, B and C were uniaxially elongated in the NMR probe. A typical evolution of the transverse magnetic relaxation function  $M_x^e(\Delta t)$  of protons attached to polymer chains in sample A is shown in Fig. 3. The sample was broken at stretching ratio values higher than 2. The initial slope of the relaxation function  $M_x^e(\Delta t)$  was considered as a suitable NMR parameter because it is well defined in this polymer system. This slope was supposed to give a good estimate of the residual energy of proton-proton interactions. Variations of the initial slope  $\Delta_e$  are reported in Fig. 4 ; they

obey a linear dependence upon the parameter  $\beta = \lambda^2 - 1/\lambda$ . Similar results also characterize samples B and C (Fig. 4).

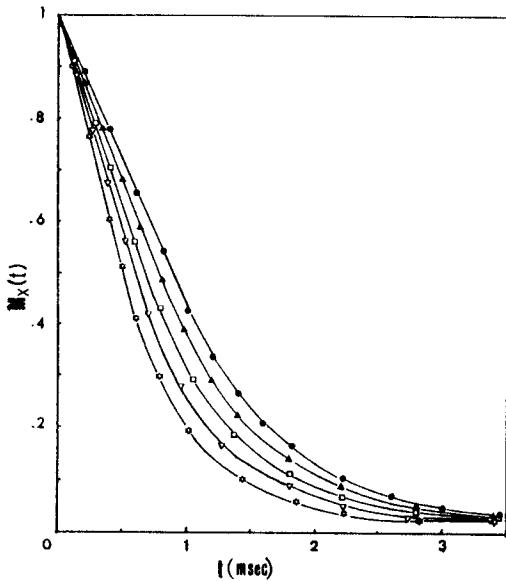


Fig. 3 - Transverse magnetic relaxation functions observed for various extension ratios  $\lambda$  from sample A. (● :  $\lambda = 1$ , ▲ :  $\lambda = 1.20$ , □ :  $\lambda = 1.40$ , ▽ :  $\lambda = 1.60$ , \* :  $\lambda = 1.90$ ).

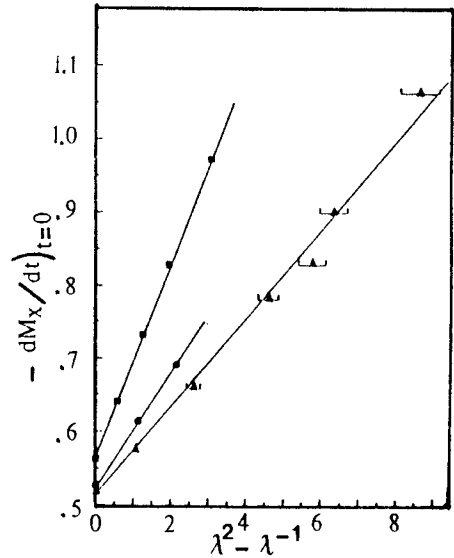


Fig. 4 - Slopes of transverse magnetic relaxation functions measured at  $t = 0$  and plotted versus  $\lambda^2 - \lambda^{-1}$  for the three samples ; ■ : sample A, ▲ : sample B, ● : sample C.

IV.a - Affine deformation

One of the most striking results, perceived from Fig. 4, concerns the linear dependence of the residual energy  $\bar{n}\Delta_e$  with respect to the difference  $\lambda^2 - 1/\lambda$ . Considering non-interacting proton pairs attached to skeletal bonds of a freely jointed chain and assuming that chain coupling junctions obey an affine Gaussian deformation, it has been recently shown that the residual energy can be expressed as a series expansion of the variable  $\lambda^2/N_e$  ( $N_e$  is the number of elementary chain bonds) (12) :

$$\Delta_e(\lambda, N_e) = \frac{0.2 \Delta_G}{N_e} \left( \lambda^2 - \frac{1}{\lambda} \right) \left( 1 - \frac{0.85 \lambda^2}{N_e} \left( 1 + \frac{1.33}{\lambda^3} \right) \right) \quad (3)$$

when the stretching direction of the gel is perpendicular to the steady magnetic field  $\vec{B}_0$ . The above formula extends to real chains except for numerical constants. In the present case, it may be asserted that chain coupling junctions in crosslinked polybutadiene undergo an affine deformation under uniaxial elongation. Thereby either of the two following assumptions can be proposed :

- i) coupling junctions do not fluctuate in time, at all :
- ii) coupling junctions fluctuate around mean positions, but fluctuations are too fast to be observed from NMR.

## IV.b - Comparison of average elementary chain lengths

Samples B and C are characterized by two different chain lengths ( $M_n = 2.4 \times 10^5$  and  $3.6 \times 10^5$ , respectively) ; but they probably have the same crosslink density. Initial slopes measured in sample B and C have about the same value  $\Delta_e^B = \Delta_e^C = 0.52 \times 10^3 \text{ rad. sec}^{-1}$ . In the absence of elongation, the magnetic relaxation function is hardly affected by chain length variations. Furthermore, the concentration of crosslinks in sample A was supposed to be about twice that characterizing samples B and C. However, the initial slope  $\Delta_e^A$  was found to be equal to  $.56 \times 10^3 \text{ rad. sec}^{-1}$ . Therefore, variations of both chain length and crosslink density have little effect on the transverse magnetization of protons. Considering now elongated samples, straight lines drawn in Fig. 4 are characterized by very different slope values. The slope  $\Sigma_\Delta^A$  was found to be  $13 \times 10^3 \text{ rad. sec}^{-1}$  in sample A, while  $\Sigma_\Delta^B = 6.5 \times 10^3 \text{ rad. sec}^{-1}$  and  $\Sigma_\Delta^C = 8 \times 10^3 \text{ rad. sec}^{-1}$ , in samples B and C, respectively. The slope  $\Sigma_\Delta$  may be considered as a parameter which helps discriminating different physical states of crosslinked polymers.

Without asserting that formula (3) is exact, it is nevertheless of interest to note that the slope  $\Sigma_\Delta^A$  is twice the slope  $\Sigma_\Delta^B$  as though  $(\Sigma_\Delta^A)^{-1}$  was a measure of the number  $N_e$  of skeletal bonds determining chain segments between consecutive coupling junctions. In this respect, samples B and C have different slope values indicating that variations of chain length affect the NMR response although these samples contain equal initial concentrations of crosslinking agent. Either of two assumptions can then be proposed :

- i) the final crosslink density is a function of chain length ;
- ii) chain ends play the role of solvent molecules giving slightly more freedom to monomeric unit motions : the ratio  $\Sigma_\Delta^C / \Sigma_\Delta^B = 1.25$  is close to the ratio  $M_n^C / M_n^B = 1.4$ .

## IV.c - Comparison with elastic moduli

Finally, the slopes  $\Sigma_\Delta^A$ ,  $\Sigma_\Delta^B$  and  $\Sigma_\Delta^C$  were compared with elastic moduli. The measured value of the elastic modulus  $G^A$  of sample A was found to be : 0.68 MPa ;  $G^B$  and  $G^C$  were equal to 0.42 and 0.63 MPa, for samples B and C, respectively. Variations of chain length and crosslink density have little effect upon the elastic modulus. This result is very contrasted to NMR observations sensitive to asymmetry properties of local monomeric unit motions. It clearly indicates that uniaxial gel elongation induces an enhancement of orientational effects of monomeric units. This enhancement is strongly dependent upon chain length and crosslink density. It probably results from intrinsic isomerisation processes of chain segments whereas weak variations of the elastic modulus reveal that this mainly depends upon monomer unit - monomer unit interactions, hardly affected by crosslink density or chain length variations. In other words, interactions of monomeric units are not stronger in sample A than in B or C although their average orientational order is much greater in the first sample.

## V. CONCLUSION

The present work illustrates a proton magnetic relaxation investigation of uniaxially elongated gels. The residual energy of spin-spin interactions proved a suitable parameter associated with semi-local properties of cross-linked polybutadiene chains. It was not the purpose of this work to give a quantitative interpretation of all results. However, it is proposed to assume that the elastic modulus is more dependent upon monomer unit - monomer unit interactions than upon elementary chain stretching. The opposite property is observed about orientational effects of monomeric units.

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