Effect of crosslinking density on the orientational order generated in strained networks: A deuterium magnetic resonance study

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The orientational order generated in uniaxially strained rubbers is investigated as a function of crosslinking density. This study was carried out on two sets of rubbers; on randomly crosslinked diene networks and on model end-linked silicone rubbers. The degree of orientational order was measured by means of the deuterium n.m.r. technique; the experiments were carried out either on dissolved deuterobenzene as an n.m.r. probe (dienes) or directly on labelled polymeric chains (silicones). The induced order increases with the crosslinking density as predicted by the kinetic description of rubber elasticity. Data are related to the thermodynamics of the networks rather than to their chemical mesh size which does not accurately describe the topological structure of interest. For both sets of samples, the degree of order varies linearly with the corresponding volume fraction of polymer at swelling equilibrium.

(Keywords: rubbers; polybutadiene; poly(dimethylsiloxane); ^{2}H nuclear magnetic resonance; orientational order; crosslinking density)

INTRODUCTION

Until recently the experimental investigations of rubbers mainly dealt with measurements of elasticity and of stress-induced birefringence. Both investigations have revealed some deviations from the kinetic description of rubber elasticity based on volumeless Gaussian chains[1,2]. For instance, it has been observed on dry rubbers that uniaxial stress and birefringence do not vary with elongation in the same manner, even at low elongations[3,4]. Additionally it has been pointed out that, for low molecular weights, the stress optical coefficient no longer remains constant with the crosslinking density[5] as expected from the classical kinetic theory. Some of these deviations have often been ascribed to correlations between chain segments in the deformed network and this is one of the reasons why various microscopic techniques are now currently used in this field for examination of elastomeric chains under deformation. Among the techniques which are sensitive to the orientational behaviour[6], deuterium n.m.r. (^{2}H n.m.r.) has emerged as a powerful tool for probing local ordering in rubbers under stress. Indeed we recall that recent ^{2}H n.m.r. experiments on constrained polymeric networks[7-9] detected an orientational anisotropy at the chain segment level yielding the corresponding order parameter; systematic studies showed that this order parameter has an explicit dependence on the extention ratio and the degree of swelling of the system.

In this work we used the same technique to study the orientational order generated in uniaxially deformed rubbers as a function of the crosslinking density i.e. the characteristic which mainly governs the elastic properties of the material. The experiments, carried out on two types of compounds, demonstrate that the induced anisotropy varies with the mesh size of the network in the same way as the volume fraction of the polymer at swelling equilibrium. This new result might have its origin in the existence of orientational correlations between chain segments in the elongated network.

EXPERIMENTAL

^{2}H n.m.r. method

The general features of ^{2}H n.m.r. in anisotropic fluids have been discussed in detail in ref. 10. 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 n.m.r. line into a doublet whose spacing $\Delta\nu$ may be written in frequency units as:

$$\Delta\nu \propto \nu_q \langle P_2(\cos\theta(t))\rangle \qquad (1)$$

where ν_q designates the static quadrupolar coupling constant ($\sim$200 KHz) and θ is the angle between the C–D bond and the direction of the macroscopic

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symmetry axis i.e. the direction of the applied tension in our case. Then the average $\langle P_2(\cos\theta(t))\rangle$ can be defined as the so-called orientational order parameter of the C–D bond relative to the symmetry axis of interest to us.

This kind of n.m.r. investigation has recently been used to study the orientational anisotropy generated in strained elastomers. From the experimental point of view, we recall that the ^{2}H n.m.r. experiments may be conveniently done on deuterated swelling agents used as probes of the polymeric environment[7] or directly on labelled polymeric chains[8,9].

Materials

In order to avoid the difficulties of synthesis of labelled networks the main part of our study has been carried out according to the first method quoted above, by using benzene-d$_6$ solubilized in diene rubbers. Nevertheless it has been possible to extend these initial experiments on deuterated probes to labelled chains of some silicone rubbers.

The diene rubbers investigated are tetrafunctional polybutadiene (PB) networks. All these networks were prepared by the Michelin Tire Company from peroxide crosslinking of a polybutadiene precursor (Diene 45 NF) whose characteristics are given in *Table 1*. The crosslinking 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 volume fraction of polymer ϕ_e at swelling equilibrium (see *Table 2*); the latter was measured at room temperature by a weighting method, using cyclohexane as a good solvent of the corresponding linear polymer. These measurements were all carried out on the samples used for the n.m.r. experiments in order to prevent any effects due to possible inhomogeneities in the primary network sheet. For guidance, *Table 2* also includes an estimation of the mean molecular weight (M_c) between adjacent network junctions derived from the corresponding values of ϕ_e through a modified Flory–Rehner type equation[11].

The other results have been obtained with end-linked poly(dimethylsiloxane) model networks, containing a known fraction of perdeuterated chains (PDMS (D)). They have been synthesized by reaction of mixtures of labelled and unlabelled α,ω-di(hydrogeno) poly(dimethylsiloxane) chains with tetra(allyloxy)ethane, used as a tetrafunctional crosslinker; the cross- or 'end-linking' reaction was carried out in toluene at a polymer volume concentration v_c (see *Table 3*). All the characteristics of these networks, including the swelling equilibrium volume fraction in cyclohexane, were reported previously[12-14].

Experimental conditions

Tension was applied to samples, the nominal dimensions of which were about 50 mm long, 8 mm wide, 1 mm thick for PB networks and 30 mm × 5 mm × 1 mm in the case of PDMS networks. Such rubbery strips were held in grips, one of which could easily be moved in order to vary the sample elongation; the stretching direction was coincident with the axis of the n.m.r. tube and the sample elongation was increased every 15 min in steps of 1 mm. The extension ratio $\lambda = L/L_0$ was determined optically by monitoring the spacings ($\simeq$25 mm) between fiducial marks to within 0.2 mm.

As indicated previously the experiments have been done either with dry samples (in case of PDMS(D)) or with slightly swollen samples (in case of PB). In the latter case, deuterated probes (C_6D_6) were dissolved in the elastomer exactly as described in ref.[7]. So each sample of the series of PB has been studied at a polymer volume fraction ϕ equal to 0.9 and it has been checked that this degree of swelling does not significantly evolve during any one experiment.

All ^{2}H n.m.r. spectra were obtained using *FT* n.m.r. equipment: a CXP 90 Brucker spectrometer operating at 2 Tesla with a conventional electromagnet; the magnetic field was perpendicular to the stretching direction.

Table 1 Characteristics of the polybutadiene precursor (Diene 45 NF)

Molecular weight		Microstructure (wt%)		
M_n	M_w	*Cis*-1,4	*Trans*-1,4	Vinyl-1,2
170 000	410 000	37	51	12

Table 2 Characteristics of the polybutadiene networks: All samples have been crosslinked in dry state using dicumyl peroxide as curing agent. ϕ_e represents the volume fraction of polymer at equilibrium (maximum) swelling in cyclohexane at room temperature. M_c refers to the mean molecular weight between crosslinks deduced from ϕ_e. p = slope of the different straight lines in *Figure 3*

Sample no.	1	2	3	4	5	6	7	8	9
ϕ_e	0.057	0.101	0.121	0.137	0.148	0.213	0.233	0.249	0.254
M_c (g mol^{-1})	97 000	37 000	27 000	22 000	19 000	9600	8000	7000	6700
$p = \dfrac{\Delta\nu}{\lambda^2 - \lambda^{-1}}$	47	73	90.5	104	112	175	193	214	201

Table 3 Characteristics of the end-linked PDMS (D) networks: M_n = molecular weight of α—ω di(hydrogen)poly(dimethylsiloxane) presursors. v_c = volume fraction of polymer at which network was generated. Φ_e was determined in cyclohexane at room temperature. p = slope of the different straight lines on *Figure 4*

Sample	A	A'	B	C
M_n (g mol^{-1})	23 000	23 000	10 500	3100
v_c	0.71	1	0.71	0.71
Φ_e	0.067	0.1	0.135	0.185
$p = \dfrac{\Delta\nu}{\lambda^2 - \lambda^{-1}}$	17	28	38	43

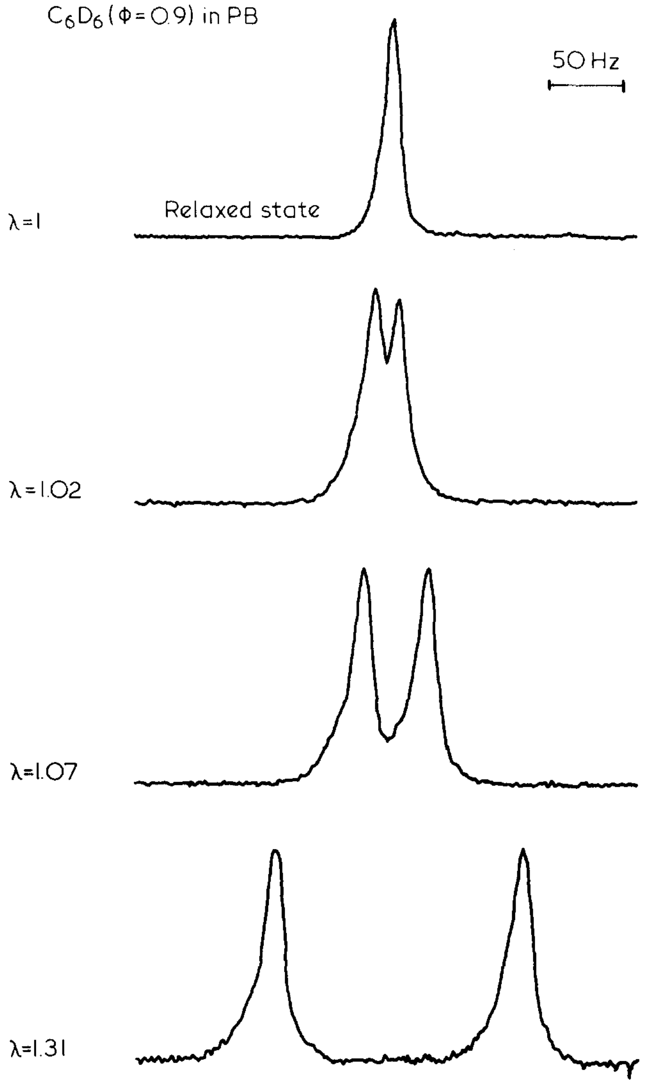

Figure 1 13 MHz ^2H n.m.r. spectra of deuterobenzene in a uniaxially strained polybutadiene network (sample No 6 in *Table 2*; polymer volume fraction ϕ=0.9) for different extension ratios λ. All spectra are the average of 100 scans

RESULTS

Figure 1 shows the change in the ^2H n.m.r. spectrum of deuterobenzene in a polybutadiene network as the sample is uniaxially elongated. The spectrum changes from a single narrow line (linewidth at half height $\delta\nu \sim 20$ Hz) in the relaxed state ($\lambda = 1$) to quadrupolar doublets ($\lambda > 1$) which are very well resolved, even at a small elongation ($\Delta\nu \neq 0$ for $\lambda \sim 1.02$)[15]. As for PDMS(D) networks, typical spectra are reported in *Figure 2*; quadrupolar doublets are still observed for $\lambda > 1$ 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.

Figures 3 and *4* illustrate the variation of the quadrupolar splittings $\Delta\nu$ with the elongation for various crosslinking densities in PB and PDMS(D) samples, respectively. It appears that the data fit with a $(\lambda^2 - \lambda^{-1})$ law as has been observed previously on a polyisoprene compound[7]; moreover the effect of the size of the network is well pronounced in both cases. The existence of such an effect on C_6D_6 (a swelling agent) suggests that the orientation of the solvent molecules is tightly coupled to that of the polymer matrix. For comparison, the right-hand ordinate in *Figure 3* gives the magnitude of the order parameter $\langle P_2 \rangle$ of the benzene C_6 axis calculated from relation (1) with $\nu_q = 190$ KHz. Finally the various slopes $p = \Delta\nu/(\lambda^2 - \lambda^{-1})$ which represent the effectiveness of the strain on the induced orientational order are reported in *Tables 2* and *3* for each sample.

DISCUSSION

We focus here on the analysis of the effect of the degree of crosslinking rather than on the ratio of elongation which has been previously discussed[7]. One striking feature of the observed averaging process is that the magnitude of the splitting $\Delta\nu$ increases with the crosslinking density for a given elongation λ. This result is in qualitative agreement with the classical description of the phenomenon[16–18] which indicates that the induced order $\langle P_2 \rangle$ has to decrease on increasing the polymer mass between chemical junctions. We recall that under the hypothesis of a Gaussian network, the expression for $\langle P_2 \rangle$ may be written in the limit of low uniaxial deformations as:

$$\langle P_2 \rangle \sim \frac{1}{N}(\lambda^2 - \lambda^{-1}) + 0(\lambda^4/N^2) \qquad (2)$$

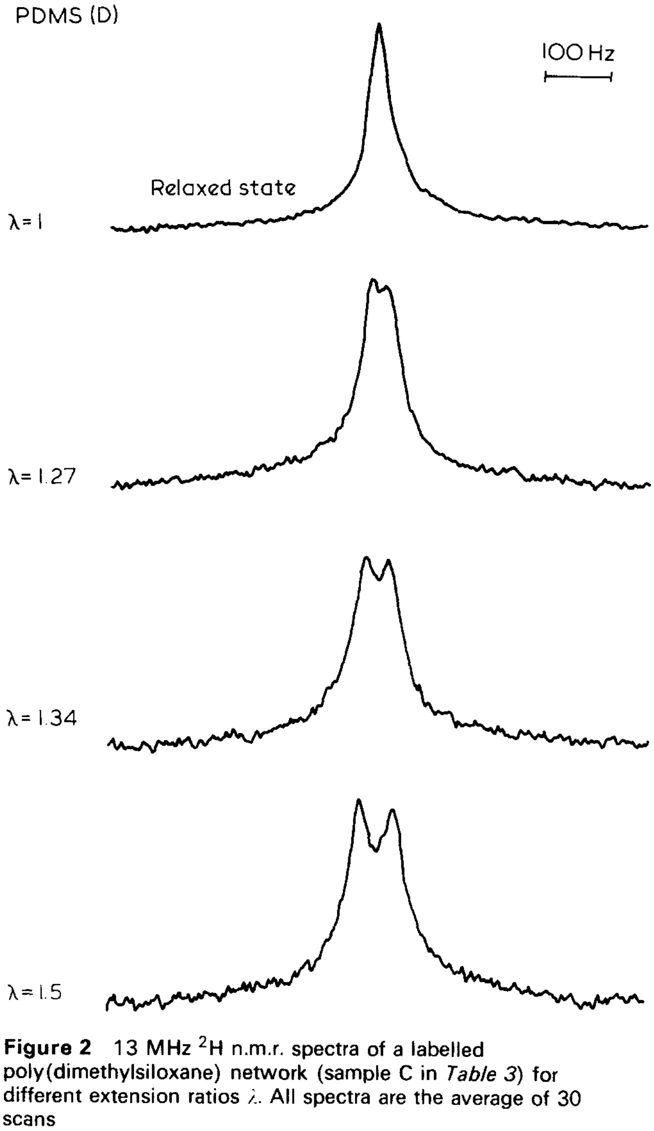

Figure 2 13 MHz ^2H n.m.r. spectra of a labelled poly(dimethylsiloxane) network (sample C in *Table 3*) for different extension ratios λ. All spectra are the average of 30 scans

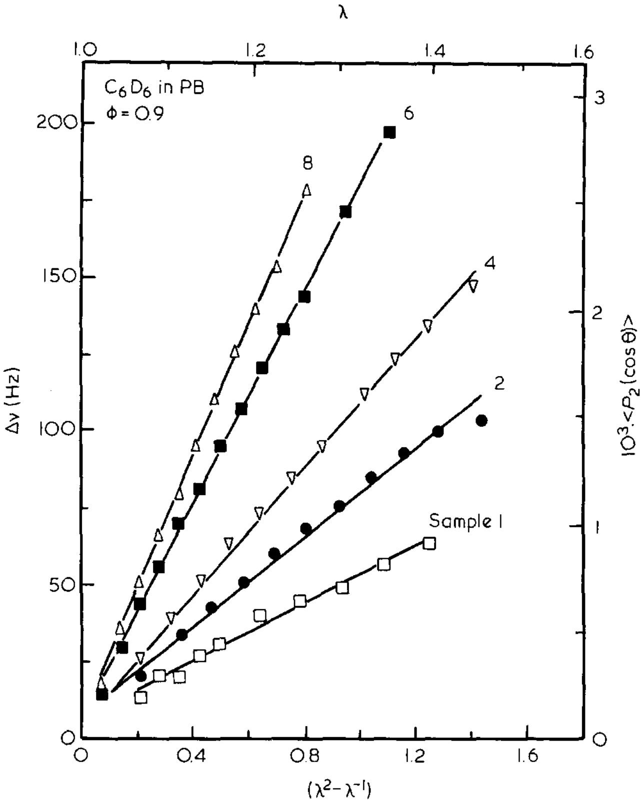

Figure 3 Quadrupolar splitting Δν (left ordinate) and calculated order parameter *S* (right ordinate) of C_6D_6 in polybutadiene networks *versus* $\lambda^2-\lambda^{-1}$ for various crosslinking densities at constant polymer volume fraction $\phi = 0.9$. For reasons of clarity, all the samples studied (see *Table 2*) have not been reported in this Figure

where *N* is the number of statistical segments per chain. However, for both types of elastomers studied, the variation of the slope *p* is lower than the one calculated from the expression (2) above: for instance, according to the *Table 2*, the ratio between the extreme values of *p* is 5 in the case of PB, while the corresponding ratio of the mass M_c is 15; in the case of PDMS a ratio of 3 has to be compared with 7 as indicated in *Table 3*.

Regarding this departure from the classical N^{-1} variation in expression (2), the experiments with 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 statistical segments of the precursor chains does not take into account the presence of trapped entanglements so that the molecular weight M_n between adjacent junctions in *Table 3* does not correctly define the network structure under interest. Indeed among the various PDMS networks, those (samples A and A′ in *Table 3*) which only differ by the value v_c of the polymer concentration during the crosslinking process and thus by the amount of trapped entanglements[20] exhibit different slopes *p*. 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 encouraged to relate the measured order parameter to the thermodynamic properties of the network, rather than to a microscopic parameter *N* which is always somewhat ill-defined for any non-ideal system. So we choose to analyse our data *versus* a *macroscopic* variable, sensitive to the topological structure of the network. For instance such a variable may be the elastic modulus *G* or the swelling equilibrium vooume fraction of the polymer Φ_e; indeed both of these characteristics of the network are sensitive to chemical and physical junctions.

In fact elasticity measurements at low deformations on the set of PB samples and data of Mark *et al.*[19] on PDMS model networks, similar to those used here, led to complex and different relationships between the slopes *p* and the corresponding Young's modulus. On the contrary, we obtained the same simple relationship between *p* and Φ_e for the two types of investigated networks: as shown in *Figures 5* and *6*, the various slopes vary linearly with Φ_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 determination of Φ_e; in fact, according to the experimental results from Candau *et al.*[20], another good solvent would not affect the linearity $\Delta\nu(\Phi_e)$ but would only modify the slope.

The linear behaviour in *Figures 5* and *6* indicates that $\Delta\nu$, and therefore the induced orientational order $\langle P_2\rangle$, is related to the network structure in the same way as Φ_e. From this point of view, experiments on PDMS(D) samples are particularly relevant because they demonstrate that the measured order $\langle P_2\rangle$, as well as the degree of equilibrium swelling Φ_e, is not related to the

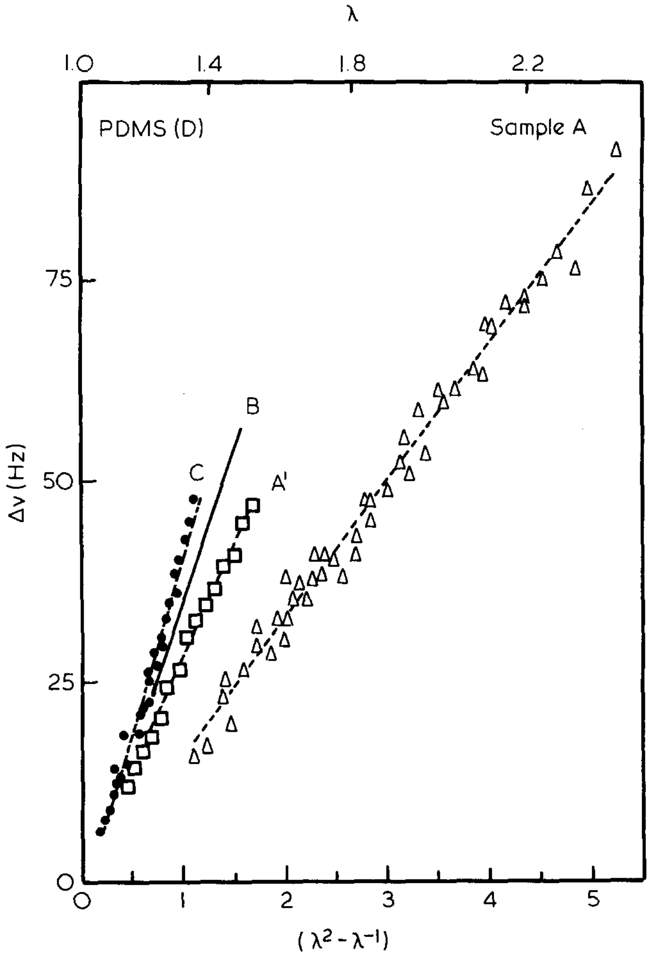

Figure 4 Quadrupolar splitting Δν of the labelled silicone networks (sample references are given in *Table 3*) *versus* $\lambda^2-\lambda^{-1}$. For reasons of clarity, data for sample B are not reported but they are aligned along the solid line indicated

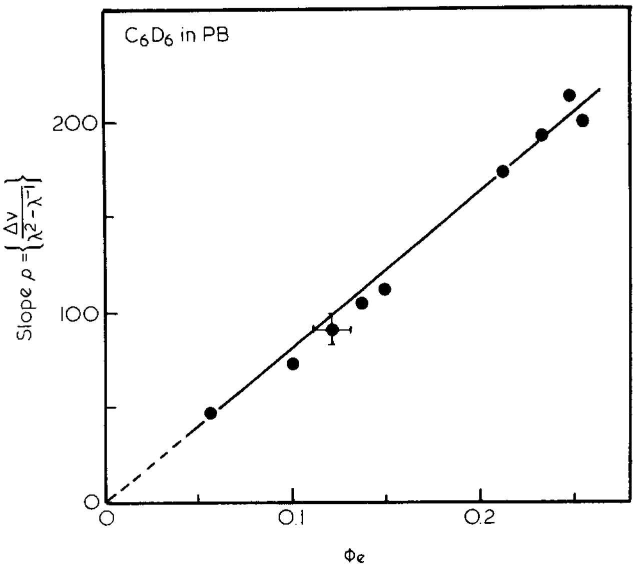

Figure 5 Slopes p of $\Delta\nu$ *versus* $\lambda^2-\lambda^{-1}$ data of *Figure 2* plotted against the swelling equilibrium fraction of polymer ϕ_e in cyclohexane for the polybutadiene networks. A linear least-square regression on a log–log scale shows that the slopes p change with $\phi_e^{1.04}$

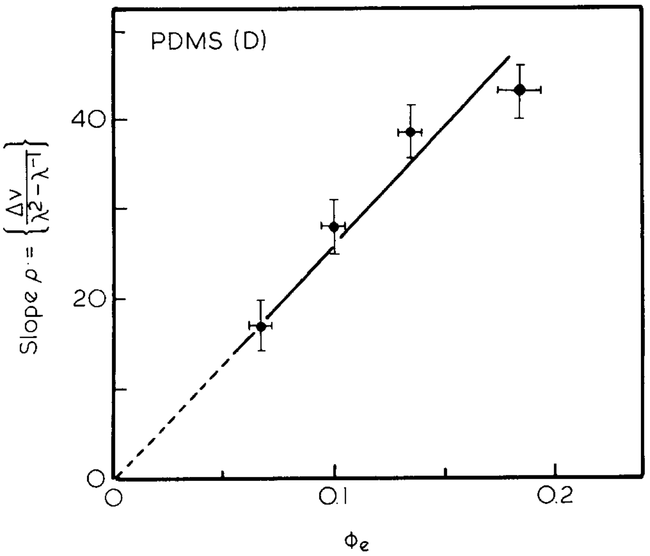

Figure 6 Slopes p of $\Delta\nu$ *versus* $\lambda^2-\lambda^{-1}$ data of *Figure 3* plotted against the swelling equilibrium fraction of polymer ϕ_e in cyclohexane for the labelled poly(dimethylsiloxane) networks. A linear least-square regression on a log–log scale shows that the slopes p change with $\phi_e^{0.93}$

presence of chemical junctions only. In fact, samples A and A′ (see earlier), exhibit different Φ_e so that the linearity is maintained. Furthermore we know from the work of Bastide *et al.*[21] on tetrafunctional networks that Φ_e, in contrast with G, is almost independent of the presence of dangling chains. Then the linear relationship in *Figures 5* and *6*, established with samples containing various densities of defects, shows that the presence of dangling chains in the network would not affect $\langle P_2\rangle$ significantly. In other words, the induced orientational anisotropy for such tetrafunctional networks is more sensitive to the density of elastic junctions than to the density of elastically effective chains, to which the Young's modulus G is directly related.

A semi-quantitative analysis of the observed relationship between $\langle P_2\rangle$ and Φ_e may be attempted by assuming that the trapped entanglements have the same efficiency in the dry state as in the swollen state. According to this crude assumption it is possible to analyse the measurements of S and Φ_e in terms of the same 'effective' mesh size characterized by the mean number of segments $N_{\rm eff}$ between junctions whether they are chemical or physical. Then we expect from the 'Φ^* theorem'[22] that Φ_e should vary as $N_{\rm eff}^{-\alpha}$ with α equal to 0.8 for lightly crosslinked networks or to 0.5 for dense networks for which excluded volume effects no longer exist[23]. In any case, the consequence of this study ($\langle P_2\rangle \propto \Phi_e$) is that the orientational order $\langle P_2\rangle$ varies with the effective mesh size more slowly than $N_{\rm eff}^{-1}$ derived from the ideal single chain approach[16]. Under these conditions, we propose that such non-classical behaviour might have its origin in the effects of orientational correlations between chain segments in the uniaxially elongated network. As has been shown experimentally[6a,7] and theoretically[24,25] the main effects of these correlations is to enhance the induced orientational anisotropy above that anticipated by the affine deformation of isolated chains. Specifically we can recall that the expression of $\langle P_2\rangle$ can be easily deduced from a phenomenological treatment where the effects of these correlations are included in the configurational entropy through a coupling between the orientation and deformation process[7]; in the limit of low deformations, we obtain:

$$\langle P_2\rangle \sim \frac{U}{N_{\rm eff}}(\lambda^2-\lambda^{-1})+O\left(\frac{\lambda^4}{N_{\rm eff}^2}\right) \qquad (3)$$

where the prefactor U is related to the strength of the coupling. Then, in the framework of this analysis, our experimental results are consistent with an enhancement factor $U(N_{\rm eff})$ increasing with $N_{\rm eff}$, i.e., $U(N_{\rm eff}) \propto N_{\rm eff}^{\beta}$ with $1-\beta$ now between 0.5 and 0.8. Concerning this point, we can recall that for networks containing mesogenic groups or for semi-rigid melts a dependence on the mesh size has already been considered theoretically for the same kind of coupling factor[26].

CONCLUDING REMARKS

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

Besides the fact that the ^{2}H n.m.r. 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 segmental ordering of the polymer. Such a coupling certainly involves orientational correlations within the deformed network. The present work emphasizes the reliability of the solvent–probe method for testing orientational phenomena in strained rubbers as we have pointed out elsewhere[37].

Finally we point out that recent neutron scattering experiments on the same PDMS(D) networks, show that the induced spatial anisotropy also exhibits a non-classical behaviour with the crosslinking density[28]. Clearly, a complete description of the response of the network to external constraints should be obtained from a close comparison of these neutron scattering results (long range configurational behaviour) with the ^{2}H n.m.r.

results (short range orientational behaviour), reported here. For instance we may yet notice that the anisotropy observed by neutron scattering, in contrast with the orientational anisotropy, appears insensitive to the polymer concentration v_c in the crosslinking process.

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Note added in proof

The relationship established herein (*Figures 5* and *6*) appears very similar to the so-called "C^*-theorem" recently established on the anisotropic part of the ^{1}H n.m.r. linewidth of swollen PDMS networks: Cohen-Addad, J. P. *et al. J. Phys.* 1984, **45**, 575.

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