Effect of dilution on the orientational order induced in strained polymer networks, as measured by ^{2}H nuclear magnetic resonance

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The orientational order generated in uniaxially strained rubbers is investigated as a function of the degree of swelling. This study is performed on polydimethylsiloxane (PDMS) networks diluted either with conventional solvents (such as chloroform) or with linear PDMS chains. Deuterium (^{2}H) nuclear magnetic resonance is used to monitor selectively the ordering of each component of the solution (the network chains or the diluent molecules). The concentration dependence of the order in the range of network volume fractions larger than 80 % is similar for both networks and diluents but depends on the nature of the diluent: the order decreases steeply when chloroform is added whereas it remains unaltered in the presence of free chains. These results mean that the orientational couplings between chain segments (introduced previously by Deloche *et al.* to account for the free chain orientation) are variably screened according to the nature of the diluent molecules. Introducing these interchain effects in a mean-field description of polymer networks allows one to discuss these observations quantitatively.

(Keywords: polydimethylsiloxane; orientational order; ^{2}H nuclear magnetic resonance; diluted networks; free chains)

INTRODUCTION

Recently, considerable effort has been devoted to developing spectroscopic techniques (infra-red dichroism, polarized fluorescence, nuclear magnetic resonance, etc.) sensitive to the microscopic chain behaviour in dense amorphous polymer systems. The aim of such an effort has been to characterize the interactions that determine the chain configurations on a local scale. Macroscopically aligned materials, such as uniaxially deformed networks, are helpful to investigate aspects of these interactions.

Deuterium nuclear magnetic resonance (^{2}H n.m.r.) studies in uniaxially strained rubbers have provided evidence that probes introduced into the network (solvent molecules[1] or polymer chains[2]) acquire an orientational order which reflects that exhibited by the network chain segments. This stress-induced orientation, and specifically that observed on free chain probes, has been attributed mainly to orientational couplings between chain segments (and solvent molecules)[3]. Short-range repulsive interactions limiting the amplitude of the reorientational motions probably dominate these couplings, so that their contribution to the chain (solvent) ordering is expected to depend on the local density of chain segments. The degree of orientational order generated in a strained rubber would thus depend on its degree of swelling and the study of this dependence might cast some light on the nature of these intersegmental interactions.

In this paper, we present preliminary ^{2}H n.m.r. studies of the concentration dependence of the stress-induced order in polydimethylsiloxane (PDMS) networks, diluted either with the usual solvent molecules or with linear PDMS free chains. Selective labelling enables us to monitor the ordering of each component of the solution (swollen network), i.e. the network chains or the swelling agents. At polymer network concentrations higher than 80 %, for a given pair of components (network plus small swelling agent or network plus diluent chain), the variation in orientational order of the diluent molecules and polymer matrix *versus* the concentration is similar. There are, however, differences according to the way of pairing the components, i.e. according to the nature of the diluent species (small rigid molecules or linear flexible chains). Thus the orientational couplings between chain segments quoted above may be increasingly or decreasingly screened, depending on the nature of the diluent. Finally, these observations are discussed within a mean-field description of rubbers that includes orientational couplings.

EXPERIMENTAL

Samples

All the experiments make use of end-linked tetrafunctional polydimethylsiloxane (PDMS) networks, whose synthesis is outlined in detail in refs. 4 and 5. Their characteristics are summarized in *Table 1*. The diluent molecules are either chloroform, which is a good solvent of PDMS, or linear PDMS free chains. The number-average molecular weight M_n of the free chains introduced in the networks is equal to or lower than that

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Table 1 Characteristics of the networks used. The two networks in each pair (unlabelled, A, B, C; labelled, A′, B′, C′) are assumed to be identical. M_n(H) and M_n(D) are the unlabelled and labelled (deuteriated) chain molecular weights. Φ_D is the fraction of perdeuteriated network chains, V_c is the polymer concentration during the crosslinking reaction and Φ_e is the polymer volume fraction at swelling equilibrium, measured in toluene

Samples	M_n(H)	M_n(D)	Φ_D	V_c	Φ_e
A	9300	–	0	0.7	0.133
A′	9900	10500	0.2	0.7	0.135
B	9300	–	0	1.0	0.169
B′	9700	10500	0.2	1.0	0.167
C	25000	–	0	1.0	0.100
C′	25000	23000	0.1	1.0	0.110

of the network chains ($M_n = 10\,500$ or 450), and in any case much lower than the critical entanglement molecular weight M_c in the melt of such materials ($M_c \simeq 17\,000$ for PDMS). The molecular weight distribution is about 1.6, for both network precursor chains and free polymer chains.

In order to observe selectively each component of the solution, i.e. the network chains or the diluent probes, we used two contrasting systems. One is a deuteriated PDMS network (PDMS(D)) (containing a known fraction of perdeuteriated chains), diluted with unlabelled molecules. The other one is an unlabelled PDMS network, diluted with labelled molecules.

Swelling process

Preweighed samples of dry PDMS network (40 mm x 6 mm x 1 mm) are exposed to the solvent vapour. The polymer volume fraction Φ is determined by weighing the samples before and after each n.m.r. experiment, assuming the additivity of polymer and solvent volumes ($\rho = 0.97\,\mathrm{g\,cm^{-3}}$ for PDMS and $1.05\,\mathrm{g\,cm^{-3}}$ for PDMS(D)). Though the experiments are performed in a capped n.m.r. tube, solvent evaporation during an n.m.r. experiment leads to a relative uncertainty $\Delta\Phi/\Phi$ of about 15%. Another major experimental difficulty comes from the fragility of the swollen networks. Thus our investigation was limited to network volume fractions ($\Phi > 0.6$) much larger than the network volume fraction at swelling equilibrium Φ_e (see *Table 1*).

Sample preparation differs when a polymer diluent is used. A drop of liquid linear PDMS chains ($T_g = -120$°C) is spread on the surface of a dry PDMS network sample at room temperature. The PDMS molten chains are short enough to be perfectly compatible with the host matrix[6,7], and free to diffuse through the network, with a diffusion coefficient[8] of about $10^{-12}\,\mathrm{m^2\,s^{-1}}$. After some days the chains have totally penetrated into the matrix and the surface of the PDMS film appears dry. The fraction of free chains introduced into the sample varies from 0 to 30%. Additional neutron scattering experiments, performed on a relaxed sample swollen at 10%, show that no effect of demixing or inhomogeneities occurs in such homopolymer solutions for that degree of swelling[9].

Stretching device

Sample elongation is performed as described earlier[3]. Both ends of the sample are gripped by jaws. One of these jaws is fixed while a calibrated screw moves the other along the n.m.r. tube. The sample elongation is monitored before and after each n.m.r. experiment with a micrometer on a microscope stage. In this fashion the elongation ratio $\lambda = L/L_0$ (where L and L_0 are the lengths of the swollen network respectively elongated and relaxed) is measured with an accuracy of about 0.2%.

N.m.r. conditions

A Bruker CXP-90 spectrometer was used, operating at 12 MHz with a conventional electromagnet (1.8 T), locked by an external proton probe. The magnetic field is normal to the uniaxially applied constraint. The temperature is regulated to 293 K (±1 K). Data are acquired after a $\pi/2$ pulse of 8 μs. The spectra are obtained by Fourier-transforming averaged free induction decays after some minor data manipulation (line broadening or trapezoidal apodization).

^{2}H N.M.R. AND ORIENTATIONAL ORDER

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

Fast anisotropic reorientations of a C–D bond lead to a quadrupolar interaction that is no longer averaged to zero[10]. Whenever motions are uniaxial around a macroscopic direction, the residual interaction splits the resonance line into a doublet whose spacing is, in frequency units:

$$\Delta\nu = \tfrac{3}{2}\nu_q P_2(\cos\Omega)\langle P_2(\cos\Theta(t))\rangle \tag{1}$$

Here ν_q denotes the static quadrupolar coupling constant ($\nu_q \simeq 200$ kHz). The angles in the Legendre polynomials characterize the experimental geometry and the molecular dynamics: Ω is the angle between the spectrometer magnetic field and the sample symmetry axis, namely the axis of the applied constraint ($\Omega = 90°$ in equation (1), so that $|P^2(\Omega)| = \frac{1}{2}$); $\Theta(t)$ is the instantaneous angle between the C–D bond and the constraint axis. The angular brackets indicate an average over the motions more rapid than the characteristic time ν_q^{-1}.

Molecular and segmental order parameters

When the angular motional average in equation (1) involves fast uniaxial intramolecular rotations around a molecular symmetry axis, one gets:

$$\langle P_2(\cos\Theta(t))\rangle = P_2(\cos\gamma)S$$

where γ is the angle between the C–D bond and the molecular axis. $S = \langle P_2(\cos\theta(t))\rangle$ is the so-called order parameter describing the anisotropy of the molecular axis reorientational motions (θ is the angle between the molecular axis and the constraint axis). Hence a measurement of the splitting $\Delta\nu$ gives direct access to the order parameter S:

$$\Delta\nu = \tfrac{3}{4}\nu_q P_2(\cos\gamma)S \tag{2}$$

The C–D bond vector itself is the local symmetry axis of the deuteriochloroform molecule, so that $\gamma = 0°$ and:

$$S(\mathrm{CDCl_3}) = \frac{4\Delta\nu}{3\nu_q} \qquad \text{with} \qquad \nu_q \simeq 168\ \mathrm{kHz}$$

In the PDMS monomer $\text{-(}Si(CD_3)_2\text{–}O\text{)-}$ the Si–C

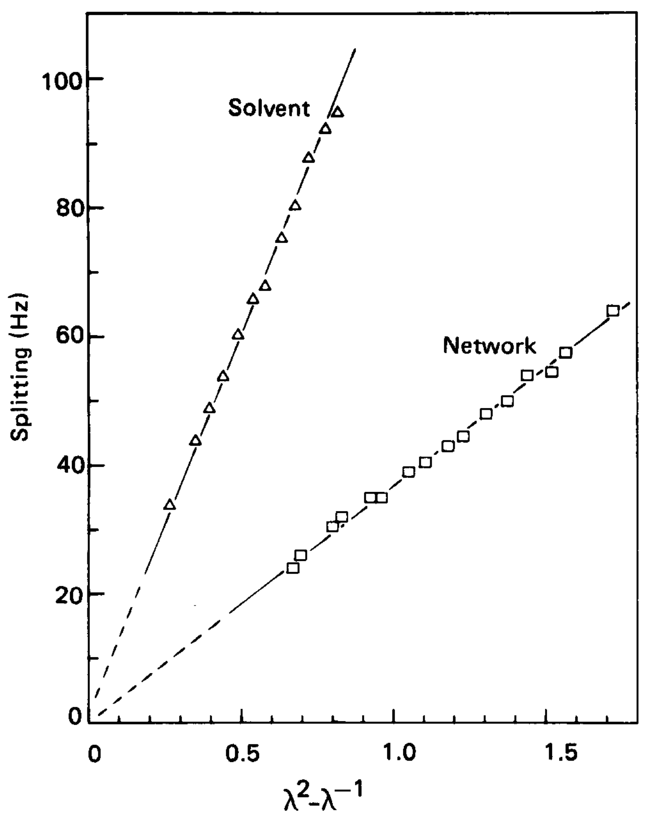

Figure 1 Quadrupolar splittings $\Delta\nu$ of a dry deuteriated polydimethylsiloxane (PDMS(D)) network under elongation (□, sample A in *Table 1*) and of deuteriochloroform ($CDCl_3$) in an elongated PDMS network (△, sample B′), as functions of $\lambda^2-\lambda^{-1}$. The polymer volume fraction is 0.8 in that latter case

vector is a symmetry axis for the methyl group rotations that involve tetrahedral angles ($\gamma=70.5°$). Then the line connecting two adjacent oxygen atoms (normal to the methyl axis, $\beta=90°$) in the PDMS chain is treated as though it were a symmetry axis for the uniaxial reorientations of the $Si\text{-}(CD_3)_2$ group. Thus, the order parameter of this particular segment is[11]:

$$S(\mathrm{PDMS})=\frac{4\Delta\nu}{3\langle P_2(\cos\beta)\rangle\langle P_2(\cos\gamma)\rangle\nu_q}=\frac{8\Delta\nu}{\nu_q}$$
$$\text{with}\quad \nu_q\simeq 175\,\mathrm{kHz} \qquad (3)$$

Including intrasegmental averaging processes (isomerization)[12] for a more realistic chain segment (one comprising several monomer units) would increase the corresponding S value as $\langle P_2(\cos\beta)\rangle$, the conformationally averaged orientation of the methyl axis relative to the segment symmetry axis, would be less than 0.5.

Induced orientational order

Previous ^{2}H n.m.r. studies performed on labelled network chains[13,14] or on deuteriated diluent probes (solvent[1] or free chains[2,15]) showed that the spectra exhibit well resolved doublets when the network is uniaxially stretched. Additional experiments carried out at a given elongation and for various angles Ω in each case lead to the Ω dependence indicated in equation (1). This demonstrates that the stress axis is a symmetry axis for the molecular dynamics.

In the low-deformation range ($\lambda<2$), the splitting $\Delta\nu$, and thus the order parameter S, depend linearly on $\lambda^2-\lambda^{-1}$, whatever the observed species, network chains[13] or probe molecules[3,16]. For instance, *Figure 1* includes data obtained on a dry PDMS(D) network and on solvent molecules. One can thus write in both cases:

$$S=P(\lambda^2-\lambda^{-1}) \qquad (4)$$

The slope P describes the efficiency of the applied constraint for inducing orientational order in the system. This order amounts to a few 10^{-3} and depends on the network properties; it varies with the crosslinking density or the trapped entanglement density in the same way as the equilibrium degree of swelling Φ_e[16,17]. The purpose of this work is to study the effect of swelling on the slope P as measured either on diluent probes or on network chains.

RESULTS

In *Figure 2a* the solvent order parameter S', characterized by the slope $P'=S'/(\lambda^2-\lambda^{-1})$, is plotted against the polymer volume fraction Φ, in the case of networks (samples A and B, see *Table 1*) swollen with deuteriochloroform ($CDCl_3$). All the reported data have been divided by the slope P obtained in the dry state ($\Phi=1$) with the deuteriated networks exhibiting the same characteristics (samples A′ and B′ respectively). This normalization allows one to compare directly the values of the order induced in solvent molecules and in chain segments (in identical networks). Clearly, the slope P' decreases regularly when the network volume fraction Φ decreases. This means that the motional averaging process observed for the solvent molecules becomes more and more efficient upon swelling (such an effect has already been observed in a polyisoprene network swollen with deuteriobenzene[1]). It remains to be determined, however, whether the observed decrease characterizes the solvent behaviour only, or reflects also a change in the orientational order of the network chains themselves.

To clarify this point, the same ^{2}H n.m.r. experiment has been repeated on the crosslinked chains, using deuteriated networks (A′ and B′) swollen with unlabelled chloroform ($CHCl_3$). The data, reported in *Figure 2b*, are normalized in the same way as previously indicated, so that the slope is equal to 1 in the dry state. A decrease of the induced ordering is also observed in that case and occurs as early as $\Phi=1$, without any threshold. However, the experimental difficulties quoted in the subsection on the swelling process limit the range of swelling. Moreover, in that case the slopes rapidly become too small compared to the spectral linewidth in the dry, relaxed state, thus limiting the range of observation to $\Phi>0.7$. Let us mention also that preliminary experiments give similar results in the case of PDMS networks swollen with benzene ($PDMS+C_6D_6$, $PDMS(D)+C_6H_6$)[18].

Different behaviour is observed when PDMS free chains are used as diluent molecules. *Figure 3* shows that the chain segment ordering measured on free chains as well as on the crosslinked network chains remains almost independent of the swelling degree at high network concentration ($0.8<\Phi<1$), and then decreases slowly at lower Φ values. In addition, the same behaviour is observed independent of the size of the free chains ($M_n=450$ or 10500).

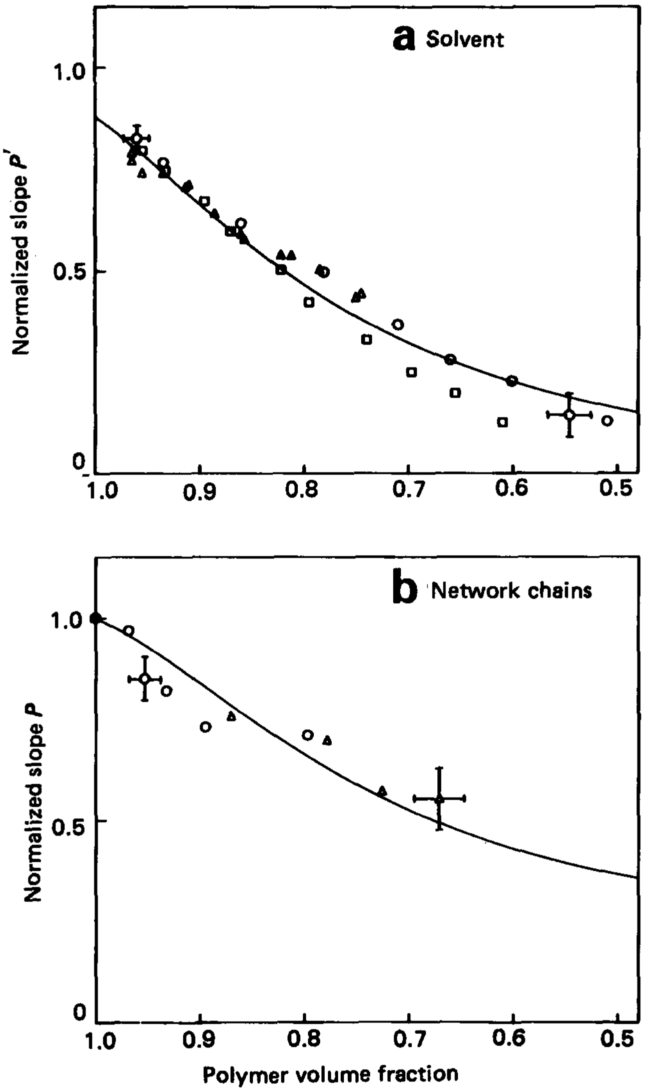

Figure 2 (a) Slopes $P'=\Delta\nu/(\lambda^2-\lambda^{-1})$ obtained on deuteriochloroform from data of the type shown in *Figure 1* (△, $CDCl_3$ in network A; ○ and □, $CDCl_3$ in network B) and (b) slopes $P=\Delta\nu/(\lambda^2-\lambda^{-1})$ obtained on deuteriated networks swollen with unlabelled chloroform (○, network A′; △, network B′ in *Table 1*), plotted against the polymer network volume fraction Φ. For each pair of networks, the reported data have been divided by the slope obtained in the dry deuterated network (networks A′ and B′, respectively). The full curves are computed from equations (11a) and (11b) with $V_{ps}=0.88$, $V_{pp}=0.92$ and $V_{ss}=0$

INTERPRETATION

Screening the orientational couplings

The induced orientation observed on both diluent molecules and network chain segments has already been attributed to local orientational couplings between the species present in the solution[1–3]. When the system is diluted, two competing effects may affect the orientational ordering:

(a) Adding a solvent to polymer chains generally increases the chain segment mobility, so that the motional averaging of the relevant nuclear interactions (quadrupolar or dipolar) is enhanced, for both chain segments and solvent molecules, resulting in lower residual interactions[19].

(b) On the other hand, diluting a polymer network induces an isotropic dilatation. As a result, the chains may be stretched out along their end-to-end vectors, which increases the segmental reorientation anisotropy and thus the residual nuclear interactions. This effect has indeed been observed by ^1H n.m.r. on highly swollen PDMS networks[20].

Observing monotonic decreases, with similar rates for the diluent molecules and for the network chains (*Figure 2*), strongly suggests that the effects related to the first process are predominant in the concentration range investigated. Specifically, adding solvent molecules releases steric motional hindrances. The propensity of a chain to align parallel to its neighbours is then lowered, or, let us say, the intersegmental orientational couplings are *screened*.

However, a striking feature of our data is that the Φ dependence of the slope *P* depends on the nature of the diluent. Indeed, contrary to the previous case, adding free chains chemically identical to the network chains does not significantly modify the system at a local scale, i.e. diluent chains do not screen orientational couplings at

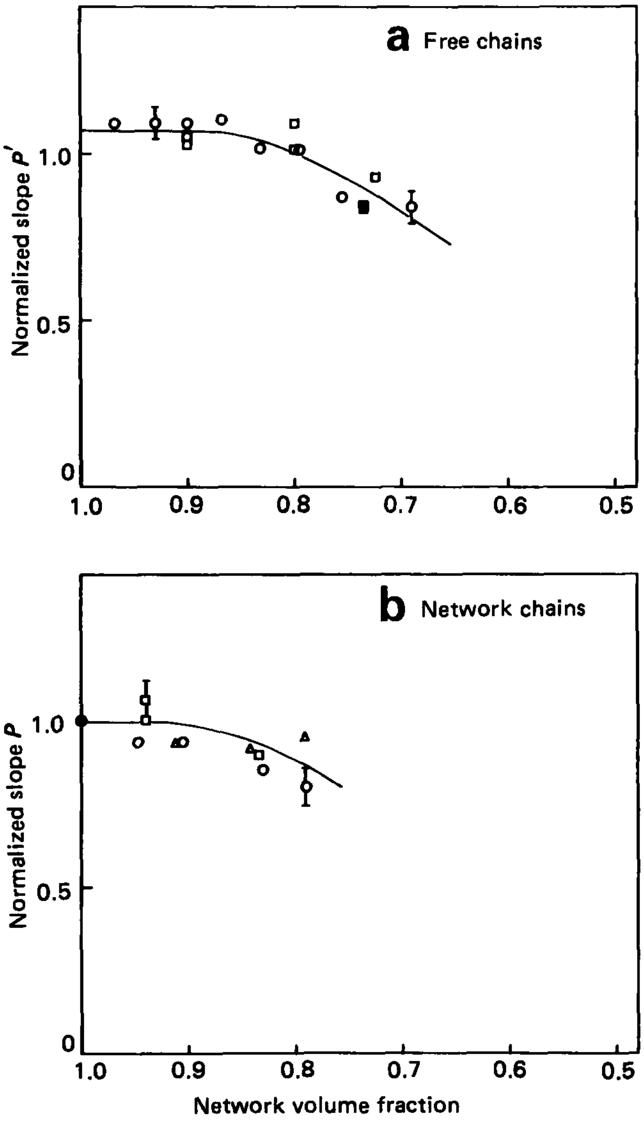

Figure 3 (a) Slopes $P'=\Delta\nu/(\lambda^2-\lambda^{-1})$ obtained on deuteriated PDMS chains (○, $M_n=450$; □, $M_n=10\,500$) dissolved in a PDMS network (sample B) and (b) slopes $P=\Delta\nu/(\lambda^2-\lambda^{-1})$ obtained on deuteriated PDMS networks diluted with unlabelled PDMS free chains (○, sample B′ diluted with oligomers ($M_n=450$); △, sample B′; □, sample C′ diluted with free chains ($M_n=10\,500$)), plotted against the polymer network volume fraction Φ. The data have been normalized as in *Figure 2*. The full curves merely show the general trend

least in the low-concentration range. Hence, our results suggest that the interchain effects under consideration come mainly from local steric effects related to the liquid-like character of the rubbery medium[21,22]. The independence of the concentration effect upon the diluent chain length (apparent in *Figure 3*) emphasizes this point. Thus, the interactions between chains may be increasingly or decreasingly screened according to whether the diluent molecules are different from or identical to the network chains.

A mean-field description

In order to make this concept of screening more quantitative, we propose to calculate explicitly the Φ dependence of the induced order through a mean-field approach, which is a direct extension of that one presented in ref. 23. The basic point is to introduce energetic terms describing local orientational couplings in a classical expression for the free energy of a swollen network[24]. The free energy F per unit volume is written as (in kT units):

$$\begin{aligned} F/\rho = {} & (1-\Phi)\int f' \ln f' \,\mathrm{d}\Omega + \Phi \int h(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R} \int f_{\boldsymbol{R}} \ln f_{\boldsymbol{R}} \,\mathrm{d}\Omega \\ & -\tfrac{1}{2}(1-\Phi)^2 U_{\mathrm{ss}} S'^2 - \tfrac{1}{2}\Phi^2 U_{\mathrm{pp}} S^2 - \Phi(1-\Phi) U_{\mathrm{ps}} S S' \\ & +(1-\Phi)\ln(1-\Phi) + \Phi(1-\Phi)\chi_0 \qquad (5) \end{aligned}$$

Here ρ is the segment density and Φ the network volume fraction. The first two terms are the orientational entropies for the solvent molecules and the network chain segments, respectively. Also, f' is the orientational distribution function of a solvent molecule, $f_{\boldsymbol{R}}$ that of a segment of a chain whose end-to-end vector is $\boldsymbol{R}$ and $h(\boldsymbol{R})$ is the distribution function of the end-to-end vectors. The three terms quadratic in S (S') are energetic terms describing orientation-dependent couplings, written in a mean-field approximation. The coefficients U_{ij} ($i,j=\mathrm{p}$ for polymer and s for solvent) are interaction energies, which may depend on temperature*. As measured in kT units, their values are expected to be less than 1 since the system does not present any spontaneous orientation. S' and S are the order parameters of the solvent and of the network chain segments, respectively. They are defined with respect to the constraint axis as:

$$S' = \int f' \left(\frac{3\cos^2\theta - 1}{2} \right) \mathrm{d}\Omega \qquad (6a)$$

$$S = \int h(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R} \int f_{\boldsymbol{R}} \left(\frac{3\cos^2\theta - 1}{2} \right) \mathrm{d}\Omega \qquad (6b)$$

where θ is the angle between the sample symmetry axis (constraint axis) and the axis of the molecule under consideration. The last two terms, the entropy of mixing and the classical Flory interaction energy, are independent of orientation and will play no role in what follows.

The orientation distribution functions are obtained by minimizing F subject to the constraints:

$$\int f' \,\mathrm{d}\Omega = \int f_{\boldsymbol{R}} \,\mathrm{d}\Omega = 1 \qquad (7)$$

$$\int f_{\boldsymbol{R}} \cos\beta \,\mathrm{d}\Omega = |\boldsymbol{R}|/Na \qquad (8)$$

where N is the number of segments per chain, a is the length associated with one segment, and β denotes the angle between a segment and the corresponding chain end-to-end vector $\boldsymbol{R}$. Following a procedure outlined in detail in the appendix, the distribution functions f' and $f_{\boldsymbol{R}}$, the partition functions, and the free energy may be obtained as functions of the parameters $V_{ij} = U_{ij}/5$ and the ratio $r^2 = R^2/R_0^2$ (ratio of the mean square end-to-end vector of a network chain to its value in the absence of constraints). We have assumed the end-to-end vectors to deform affinely. The integral over the distribution $h(\boldsymbol{R})\,\mathrm{d}\boldsymbol{R}$ has been replaced by a sum over the three directions in space (x,y,z), considering additionally that all the end-to-end vectors have the same length in the relaxed. state. The result can be written:

$$\begin{aligned} F_{\mathrm{v}}/\rho = {} & \tfrac{1}{2}A_{\mathrm{ss}}(1-\Phi)^2 S'^2 + \tfrac{1}{2}A_{\mathrm{pp}}\Phi^2 S^2 + A_{\mathrm{ps}}\Phi(1-\Phi)SS' \\ & + (\Phi/2N) r^2(\lambda^2 + 2\lambda^{-1}) + (3\Phi/20N^2) r^4(\lambda^4 + 2\lambda^{-2}) \\ & - (\Phi/N) r^2(\lambda^2 - \lambda^{-1})[V_{\mathrm{pp}}\Phi S + V_{\mathrm{ps}}(1-\Phi)S'] \qquad (9) \end{aligned}$$

The first three terms are the local coupling terms; the parameters A_{ij} are screened as compared to the bare interaction parameters U_{ij}; their explicit Φ dependence is given by:

$$\begin{aligned} A_{\mathrm{ss}} &= 5[V_{\mathrm{ss}} - (1-\Phi)V_{\mathrm{ss}}^2 - \Phi V_{\mathrm{ps}}^2] \\ A_{\mathrm{pp}} &= 5[V_{\mathrm{pp}} - \Phi V_{\mathrm{pp}}^2 - (1-\Phi)V_{\mathrm{ps}}^2] \qquad (10) \\ A_{\mathrm{ps}} &= 5[V_{\mathrm{ps}} - \Phi V_{\mathrm{pp}} V_{\mathrm{ps}} - (1-\Phi)V_{\mathrm{ps}} V_{\mathrm{ss}}] \end{aligned}$$

The structure of each of these expressions is easily understandable in the framework of such a mean-field model:

(a) The first term, linear in V_{ij}, comes from the orienting energy introduced in equation (5) (contribution $-U_{ij}/2$) and from the disorienting entropy.

(b) The other terms, quadratic in the V_{ij}, may be viewed as effective interaction energies between two molecules via a third one, weighted as expected by the concentration of the latter.

The two additional terms in equation (9) represent the classical entropic elasticity of a swollen network, including the first non-Gaussian term in r^4/N^2. The last term expresses a coupling between the deformation and the orientations of both the network chain segments and the solvent molecules. The equilibrium order parameters S and S' are then computed by minimizing F at fixed λ and Φ:

$$\partial F/\partial S = 0 \quad \text{and} \quad \partial F/\partial S' = 0$$

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*The V_{ij} parameters can be viewed as orientation-dependent corrections to the usual interaction parameters $\tilde{\chi}_{ij}$. Expanding the $\tilde{\chi}_{ij}$ in powers of S and S', one gets:

$$\begin{aligned} \tilde{\chi}_{\mathrm{ss}} &= \chi_{\mathrm{ss}} + \tfrac{1}{2}S'^2 U_{\mathrm{ss}} \\ \tilde{\chi}_{\mathrm{pp}} &= \chi_{\mathrm{pp}} + \tfrac{1}{2}S^2 U_{\mathrm{pp}} \\ \tilde{\chi}_{\mathrm{ps}} &= \chi_{\mathrm{ps}} + SS' U_{\mathrm{ps}} \end{aligned}$$

One obtains equation (4), the Flory parameter χ_0 being defined as usual by $\chi_0 = \chi_{\mathrm{ps}} - \tfrac{1}{2}(\chi_{\mathrm{ss}} + \chi_{\mathrm{pp}})$

This leads to the following expressions:

$$S' = S_0 r^2 \frac{\Phi V_{ps}}{1 - \Phi V_{pp} - (1-\Phi)V_{ss} + \Phi(1-\Phi)(V_{pp}V_{ss} - V_{ps}^2)} \quad (11a)$$

$$S = S_0 r^2 \frac{1-(1-\Phi)V_{ss}}{1 - \Phi V_{pp} - (1-\Phi)V_{ss} + \Phi(1-\Phi)(V_{pp}V_{ss} - V_{ps}^2)} \quad (11b)$$

where $S_0 = 1/5N(\lambda^2 - \lambda^{-1})$ is the classical expression for the average order induced in a dry uniaxially stretched network[25] in the absence of local coupling terms. S_0 is the only factor that depends on the network characteristics, via N. Each of these expressions exhibits two Φ-dependent factors. One is related to the chain dimension $r^2(\Phi)$, which varies as $\Phi^{-2/3}$ according to an affine description of the swelling[25]. The other factor expresses the effects of the local interactions.

A similar approach can be used when free chains are dissolved in the network, assuming that free chain segments play the same role as the solvent molecules. In that case, the expressions (11a) and (11b) simplify, since the chemical identity of free chains and network chains leads to identical parameters V_{ij} ($V_{pp} = V_{ps} = V_{ss} = V$):

$$S' = S_0 r^2 \Phi V/(1-V) \quad (12a)$$

$$S = S_0 r^2 [1 + \Phi V/(1-V)] \quad (12b)$$

The free energy in that case is written as:

$$F/\rho = \tfrac{1}{2}A\langle S\rangle^2 + (\Phi/2N)r^2(\lambda^2 + 2\lambda^{-1}) + (3\Phi/20N^2)r^4(\lambda^4 + 2\lambda^{-2}) - (\Phi(N)r^2(\lambda^2 - \lambda^{-1})V\langle S\rangle \quad (13)$$

where $A = V - V^2$ and $\langle S\rangle = \Phi S + (1-\Phi)S'$. An expression of this form was inferred in ref. 3. Physically, expressing F as a function of $\langle S\rangle$ (which may represent an order parameter averaged over all the segments present in the system) casts some light on the fact that free chains and network chains are locally indistinguishable in our description. Noticeably, the interaction constant A no longer depends on Φ: there is no screening effect in that case.

Comparison with experimental results

The spirit of our model is to try to fit the data for each polymer–solvent pair with one set of V_{ij} parameters only. In a first step, the factor $r^2(\Phi)$ is supposed to vary as $\Phi^{-2/3}$. The parameter V_{ps} is determined by a direct extrapolation of the ratio $S'(\Phi)/S(\Phi)$ at zero solvent concentration ($\Phi = 1$). V_{ss} is assumed to be negligible compared to V_{pp} and V_{ps} for chloroform, whose molecules do not exhibit any spontaneous orientation. V_{pp} is then the unique adjustable parameter. The full curves in *Figure 2* show that the expressions (11a) and (11b), with $V_{ps} = 0.88 \pm 0.05$ and $V_{pp} = 0.92 \pm 0.02$, do reproduce the variation of the induced order in the range of swelling investigated. The calculated data have been normalized in the same way as the experimental ones (by dividing them by the slope obtained for the network chains in the dry state $S_0/(1 - V_{pp})$ (cf. equation (11b)).

The same procedure may be used in the case of networks diluted with free chains. Using the *same* value of $V = V_{pp}$ ($= 0.92$), the Φ dependences calculated from the equations (12a) and (12b) are reported in *Figure 4* together with the data obtained on a network diluted with oligomers (cf. *Figure 3*). The practically constant curve contrasts strongly with the previous case and is in good agreement with the observed Φ variation, in the range $\Phi \gtrsim 0.8$. The discrepancy in the observed and calculated magnitudes of the induced orders in *Figure 4a* may be due to intrinsic differences in the two networks used (samples B and B′), which thus far have been assumed to be strictly identical. Hence this discrepancy is not considered to be relevant to the present discussion.

Discussion

The mean-field description accounts for the two regimes observed for each of the two kinds of diluent: a steep decrease in the case of solvent molecules, and a quasi-plateau for $\Phi > 0.85$ in the case of free diluent chains.

The values of V_{pp} and V_{ps} appear to be large, reflecting a

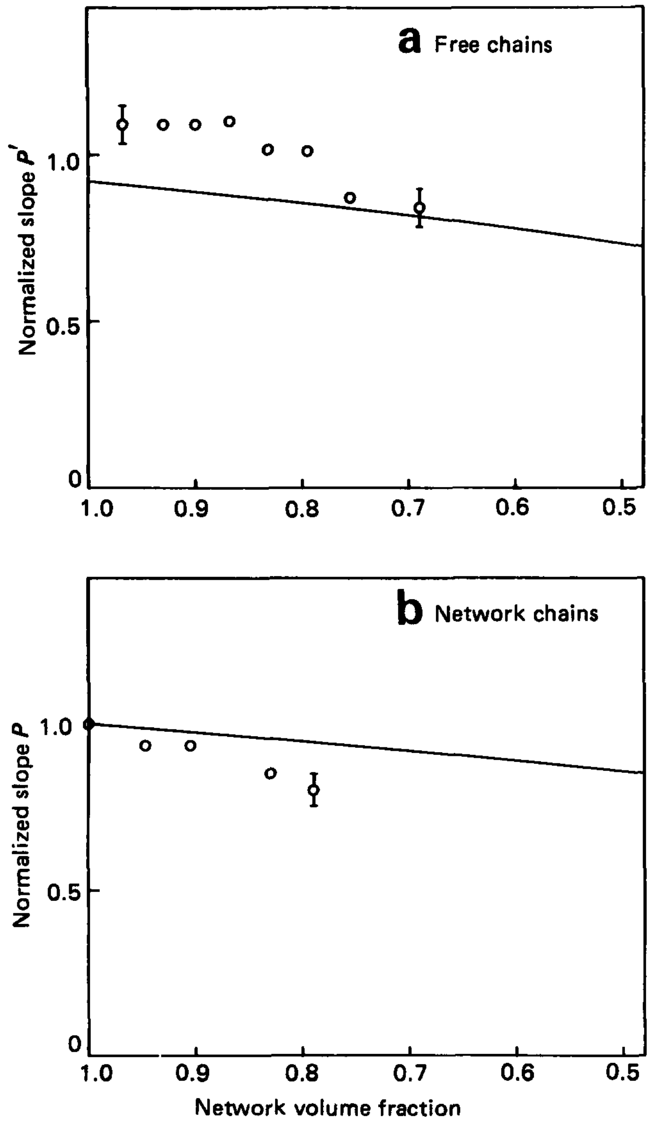

Figure 4 (a) Slopes $P' = \Delta\nu/(\lambda^2 - \lambda^{-1})$ obtained on deuteriated oligomers ($M_n = 450$) dissolved in a PDMS network (sample B) and (b) slopes $P = \Delta\nu/(\lambda^2 - \lambda^{-1})$ obtained on a deuteriated PDMS network (sample B′) diluted with unlabelled PDMS oligomers, plotted against the polymer network volume fraction Φ (the same data as on *Figure 3*). The full curves have been computed from equations (12a) and (12b) respectively, using the previous value $V_{pp} = 0.92$

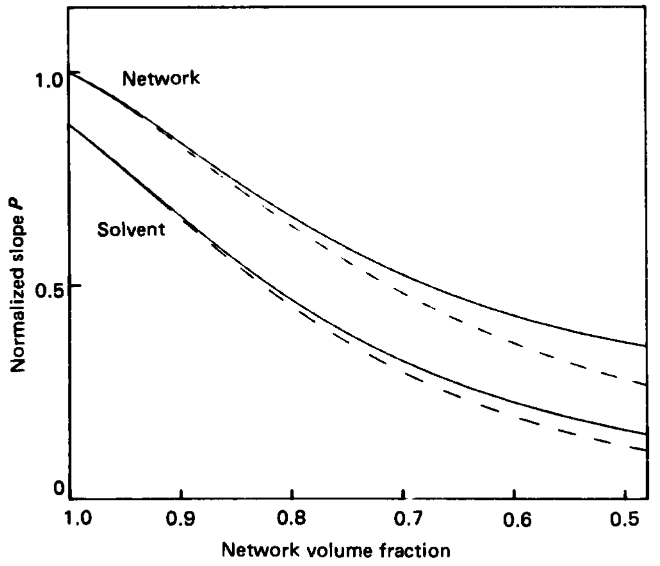

Figure 5 Reduced orientation $S(\Phi)/S(\Phi=1)$ computed from equations (11) for the solvent (lower curves) and for the network (upper curves), including the factor $r^2(\Phi) \sim \Phi^{-2/3}$ (full curves) or excluding this factor (broken curves). The V_{pp} value is 0.92 in the first case and 0.90 in the second one

strong coupling situation*. Indeed, as has been noted above, the value unity would correspond to a divergence in equations (11) and (12), i.e. to a spontaneous orientation in the system. Thus, the data as a whole emphasize the dominance of local orientational couplings in the conventional end-to-end stretching of the network chains. Specifically, the fact that the order parameters measured on network chains and on free chains have the same order of magnitude is well accounted for by the value attributed to V ($V \simeq 1$). Indeed, the term $\Phi V/(1-V)$ in equation (12b) becomes dominant in that case, so that $S' \simeq S$.

The role of the factor $r^2(\Phi)$ remains to be discussed. As quoted above, this factor varies as $\Phi^{-2/3}$ in an affine description of the swelling (which probably overestimates the end-to-end vector extension[27]). Another case, which is perhaps also unrealistic, would be to consider that $r^2(\Phi) \equiv r_0^2$. In *Figure 5* we contrast the induced order computed in these two extreme cases for a network swollen with solvent molecules. Clearly, good agreement with the experimental data may be obtained in both cases with only slightly different values of V_{pp} ($V_{pp}=0.92$ and $V_{pp}=0.90$). On the contrary, in the case of networks diluted with free chains, it is clear from equations (12a) and (12b) that the Φ dependence arising from the $\Phi^{-2/3}$ factor balances that due to the mean-field treatment, and thus cannot be ignored. This may be related to one of the inadequacies in the modelling, which can be reviewed by considering the following points:

(a) The first obvious deficiency concerns the neglect of the connectivity between the segments of a diluent chain; this connectivity may introduce additional hindrances in the free chain segment's reorientational motion.

(b) Another limitation, inherent to the mean-field treatment itself, is neglecting all fluctuations in the model; this will lead to an overestimation of the interaction energies. Introducing fluctuations would indeed shift the divergence in (11) and (12) farther from the values attributed to the V_{ij} and so would lessen the relative strength of the couplings. As pointed out at the end of the subsection on molecular and segmental order parameters, considering a more realistic chain segment (smaller value of $\langle P_2(\cos\beta)\rangle$ in equation (3)) would enhance the order parameter of the network chains, and thus would also lower the parameter V_{ps} and in turn V_{pp}. However, fitting the free chain behaviour may turn out to be worse in that case.

Moreover, the order parameter S is obtained as an ensemble average over the crosslinked chains whereas the observed order corresponds to a time average at the segmental level. However, as it appears in equations (20a) and (20b) in the appendix, S is the sum of two terms. The first one comes from the end-to-end stretching and describes an anisotropy along each end-to-end vector. The second one arises from the self-consistent orientational field and is the same for all the chains. This latter term describes the uniaxiality established in the system and is the dominant process in our situation of strong coupling.

CONCLUDING REMARKS

These results as a whole demonstrate that the orientational order induced in strained networks is mainly related to the nature of the local chain confinement, that is, the density of near-neighbour segmental interactions. They suggest that this confinement is minimally perturbed when free chains are introduced into the networks. However this confinement is sensitive to the addition of a small, foreign diluent.

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APPENDIX

The orientation-dependent part of the free energy per unit volume is written as (in kT units):

$$F/\rho = \tfrac{1}{3}\Phi\sum_{\alpha}\int f_\alpha \ln f_\alpha \, \mathrm{d}\Omega + (1-\Phi)\int f' \ln f' \, \mathrm{d}\Omega - \tfrac{1}{2}\Phi^2 U_{pp} S^2$$
$$- \tfrac{1}{2}(1-\Phi)^2 U_{ss} S'^2 - \Phi(1-\Phi) U_{ps} S S' \qquad (14)$$

where the notation is specified in the text and $\alpha = x,y,z$. The constraints (7) are implicit in the normalization of the distribution functions, whereas the constraint (8) must be taken into account by introducing a Lagrange multiplier μ_α (note that μ_α has the dimension of a force):

$$\mathscr{F}/\rho = F/\rho + \tfrac{1}{3}\Phi\sum_{\alpha}\mu_\alpha \int f_\alpha \cos\beta_\alpha \, \mathrm{d}\Omega \qquad (15)$$

The orientation distribution functions f_α and f' are obtained by specifying that $\mathscr{F}$ is minimal for every

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* In the case of rigid-rod molecules dissolved in polyisoprene networks, the V_{ps} values derived from fluorescence polarization experiments reflect weaker couplings (V_{ps} between 0.1 and 0.5, according to rod size)[26]

variation of f_α and f'. We thus obtain:

$$f_\alpha = Z_\alpha^{-1}\exp[\tfrac{3}{2}\Phi U_{pp}S\cos^2\theta + \tfrac{3}{2}(1-\Phi)U_{ps}S'\cos^2\theta + \mu_\alpha\cos\beta_\alpha] \tag{16a}$$

$$f' = Z'^{-1}\exp[\tfrac{3}{2}(1-\Phi)U_{ss}S'\cos^2\theta + \tfrac{3}{2}\Phi U_{ps}S\cos^2\theta] \tag{16b}$$

where Z' and Z_α are the partition functions determined by:

$$Z_\alpha = \int d\Omega\exp\{[\Phi V + (1-\Phi)W]\cos^2\theta + \mu_\alpha\cos\beta_\alpha\} \tag{17a}$$

$$Z' = \int d\Omega\exp\{[(1-\Phi)V' + \Phi W']\cos^2\theta\} \tag{17b}$$

where $V = \frac{3}{2}U_{pp}S$, $V' = \frac{3}{2}U_{ss}S'$, $W = \frac{3}{2}U_{ps}S'$ and $W' = \frac{3}{2}U_{ps}S$, S and S' being the order parameters for the network and the solvent, respectively.

One can carry out the calculation of Z_α and Z' by assuming that μ_α, V, V', W and W' are small. We thus obtain Z_α and Z' as expansions in powers of μ_α^2 and the coefficients V and W (V' and W'):

$$Z_z = 4\pi\left(1 + \frac{q}{3} + \frac{\mu_z^2}{6} + \frac{q^2}{10} + \frac{q^3}{42} + \frac{\mu_z^2}{10} + \frac{\mu_z^2 q^2}{28} + \frac{\mu_z^4}{120} + \frac{\mu_z^4 q}{168}\right) \tag{18a}$$

$$Z_x = Z_y = 4\pi\left(1 + \frac{q}{3} + \frac{\mu_x^2}{6} + \frac{q^2}{10} + \frac{q^3}{42} + \frac{\mu_x^2 q}{30} + \frac{\mu_x^2 q^2}{140} + \frac{\mu_x^4}{120} + \frac{\mu_x^4 q}{840}\right) \tag{18b}$$

$$Z' = 4\pi\left(1 + \frac{q'}{3} + \frac{q'^2}{10} + \frac{q'}{42}\right) \tag{18c}$$

where $q = \Phi V + (1-\Phi)W$ and $q' = \Phi W' + (1-\Phi)V'$ (Z' is obtained by putting $\mu_\alpha = 0$ in Z_α). We then obtain $r'_\alpha = R_\alpha/Na$ from

$$r'_\alpha = \frac{1}{Z_\alpha}\frac{\partial Z_\alpha}{\partial\mu_\alpha}$$

as a function of q and μ_α. By inverting the preceding relation, we can obtain μ_α as a function of r'_α and q, and substitute it in the expression for Z_α. The results are:

$$Z_z = 4\pi\left(1 + \frac{q}{3} + \frac{q^2}{10} + \frac{3r_z'^2}{2} + \frac{r_z'^2 q}{10} + \frac{99r_z'^4}{40}\right) \tag{19a}$$

$$Z_x = 4\pi\left(1 + \frac{q}{3} + \frac{q^2}{10} + \frac{3r_x'^2}{2} + \frac{7r_x'^2 q}{10} + \frac{99r_x'^4}{40}\right) \tag{19b}$$

The distribution functions f' and f_α are therefore expressed as functions of $r_\alpha'^2$ and q (q'). Introducing these expressions in F, we get the expression (9) in the text. S_α and S' are then given by:

$$S_z = \tfrac{3}{5}r_z'^2 + \tfrac{2}{15}q \tag{20a}$$

$$S_x = -\tfrac{3}{10}r_x'^2 + \tfrac{2}{15}q \tag{20b}$$

$$S' = \tfrac{2}{15}q' \tag{20c}$$

S_x and S_z contain a contribution due to the constraints imposed on chain extremities, and another one arising from the local couplings (the q terms), which is the same in each expression.

Note that the first non-Gaussian term in r^4/N^2 may be of the same order of magnitude as the coupling term $-(\Phi/2N)r^2(\lambda^2-\lambda^{-1})[V_{pp}\Phi S + V_{ps}(1-\Phi)S']$, and then must be included in (9).

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