

Orientation and anisotropy of dangling chains in a deformed network

Burak Erman*, Jean-Pierre Queslelt and Lucien Monneriet†

Laboratoire de Physicochimie Structurale et Macromoléculaire, Associé au CNRS, ESPCI,
10 rue Vauquelin, 75231 Paris Cedex 05, France

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The segmental orientation of dangling chains in a uniaxially stretched *cis*-1,4-polyisoprene network is determined by fluorescence polarization measurements. The results show that the dangling chains are orientationally coupled, very strongly, to the network chains over a wide range of extension ratios. Calculations performed on the basis of freely jointed chains show, however, that the change in the overall dimensions of dangling chains should be negligibly small. This indicates that the measured segmental orientation is a local effect and does not imply anisotropy of the overall dimensions of these molecules. These observations are in agreement with recent results of nuclear magnetic resonance and neutron scattering experiments on poly(dimethylsiloxane) networks containing free molecules.

(Keywords: *cis*-1,4-polyisoprene; fluorescence polarization; dangling chains; segmental orientation; local orientational coupling)

INTRODUCTION

Segmental orientation in a network under simple elongation is customarily represented by the orientation function S as:

$$S = (3\langle \cos^2 \theta \rangle - 1)/2 \quad (1)$$

where θ is the angle between the direction of the segments and the direction of extension. Angular brackets denote averaging over all segments of interest. In the present paper, we report results of orientation measurements of dangling *cis*-1,4-polyisoprene chains and compare their orientation with those of the network chain segments. The comparison may conveniently be made by defining a coupling function f as:

$$f = S_d/S \quad (2)$$

where S_d and S are the orientation functions for the dangling and network chains, respectively. The function f may vary between 0 and 1, where the latter denotes complete orientational coupling of the dangling chains to the network chains, and the former indicates that there is no orientational coupling between the two.

MATERIALS AND METHODS

Samples were generously provided by Manufacture Michelin.

Binodal networks were formed from blends of 75 wt % of an anionic commercial polyisoprene (Shell IR 307) with a high *cis*-1,4 configuration (92% *cis*, 5% *trans*) ($T_g(\text{d.s.c.}) = -60^\circ\text{C}$) of high molecular weight

($M_n = 46.3 \times 10^4$, $M_w = 182 \times 10^4 \text{ g mol}^{-1}$) and 25% of polyisoprene chains of low molecular weight ($M_n = 50\,000$), the microstructure of which is similar to that of IR 307.

Anionic polyisoprene chains were labelled in the centres by using a method analogous to that reported previously for polystyrene¹. Monofunctional 'living' chains of molecular weight 300 000 were synthesized and deactivated by 9,10-bis(bromomethyl)anthracene. Each of the resulting chains of double molecular weight contains a dimethylantracene fluorescent group at its centre. Thus the fluorescent transition moment, the orientation of which is measured, lies along the chain axis.

Polyisoprene chains were labelled at their ends by deactivation of monofunctional 'living' chains of molecular weight 600 000 with 9-bromomethylantracene. The centre-labelled or the end-labelled polymer (1%) and the matrix (99%), carefully purified by extraction with ethanol, were mixed in solution.

Samples were moulded and crosslinked with dicumyl peroxide. Crosslinking densities were characterized by the average molecular weight M_c of network chains (between adjacent junctions) derived from measurements of the equilibrium swelling ratio in cyclohexane and through the classical Flory–Rehner equation. Values of M_c were 2.2×10^4 and $2.1 \times 10^4 \text{ g mol}^{-1}$ for samples containing centre-labelled and end-labelled polymers, respectively. The comparison of these values of M_c with the precursor molecular weight of the labelled chains (600 000) ensured that the anthracene group was after the crosslinking process either in the backbone of active chains of the network or at the end of dangling chains. The fluorescence polarization apparatus has been described elsewhere². Measurements of nominal stress and anthracene orientation S as a function of extension ratio α (defined as the ratio of the deformed length to the undeformed length of the sample) were carried out during uniaxial stretching at constant crosshead speed, $V = 50 \text{ mm min}^{-1}$, and at a temperature of 298 K.

* Permanent address: Bogazici University, Bebek, Istanbul, Turkey

† Present address: Manufacture Française des Pneumatiques Michelin, Centre d'Essais et de Recherche de Ladoux, 63040 Clermont-Ferrand, France

‡ To whom correspondence should be addressed

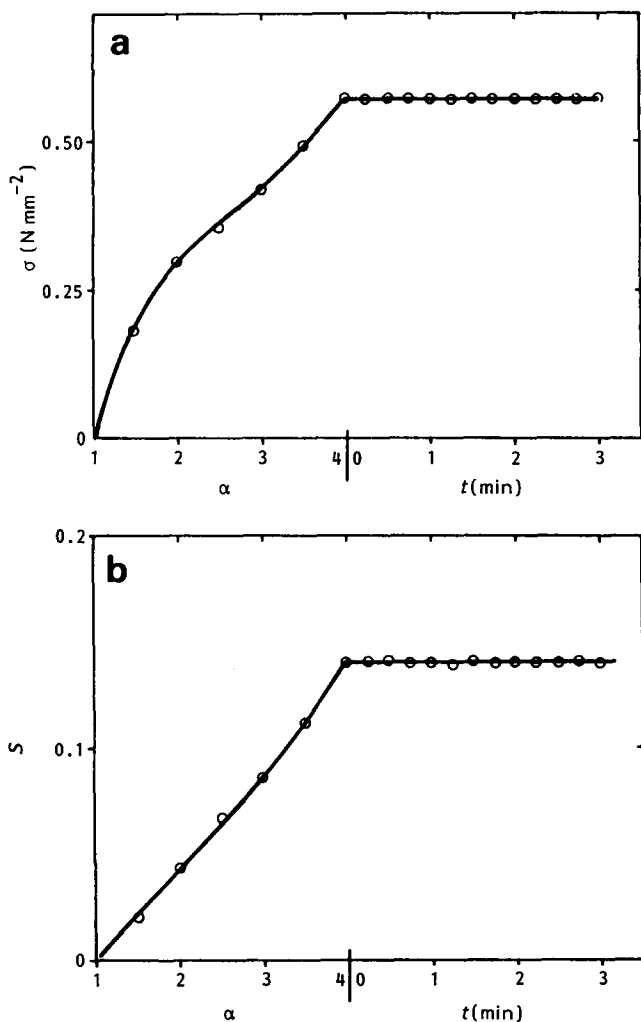


Figure 1 Nominal stress σ and orientation function S for the sample with labelled dangling chains versus extension ratio α during uniaxial stretching at constant crosshead speed and versus time during relaxation at $\alpha=4$

RESULTS

Nominal stress σ and orientation function S for the sample containing end-labelled dangling chains are reported in *Figure 1* as functions of extension ratio during uniaxial stretching at constant crosshead speed and as functions of time during subsequent relaxation at $\alpha=4$. No relaxation of either stress or orientation occurs. It can be deduced therefore that data presented in this paper were equilibrium data.

The measured orientation functions for the network and dangling chains are presented in *Figure 2* as a function of extension ratio α . Full circles represent data points for the network chains and the open circles are for the dangling chains. The full curve is fitted to the full circles. The broken curve indicates the deviation of the orientation of dangling chains from those of the network chains at high values of α .

The coupling function is presented in terms of extension ratio in *Figure 3*. However, in order for the coupling function given by equation (2) to be meaningful, measurements of S_d and S must be performed on networks with the same M_c . If the M_c values of the networks being compared are different, a correction to f is required by taking into consideration the inverse dependence^{3,4} of the orientation function on M_c . In the

present experiments S_d and S were measured on networks with $M_c=2.1 \times 10^4$ and 2.2×10^4 , respectively. The ordinate values in *Figure 3* represent the corrected coupling function f_{corr} obtained according to the relation:

$$f_{\text{corr}} = (M_{c,1}/M_{c,2})(S_d/S) \quad (3)$$

where $M_{c,1}=2.1 \times 10^4$ and $M_{c,2}=2.2 \times 10^4$. The points obtained in this manner indicate that coupling is very strong, being ca. 0.96–0.97 for values of α between 1 and 5. The curve through the experimental points indicates that the degree of coupling is independent of extension up to $\alpha=5$ and shows a progressive decrease at higher

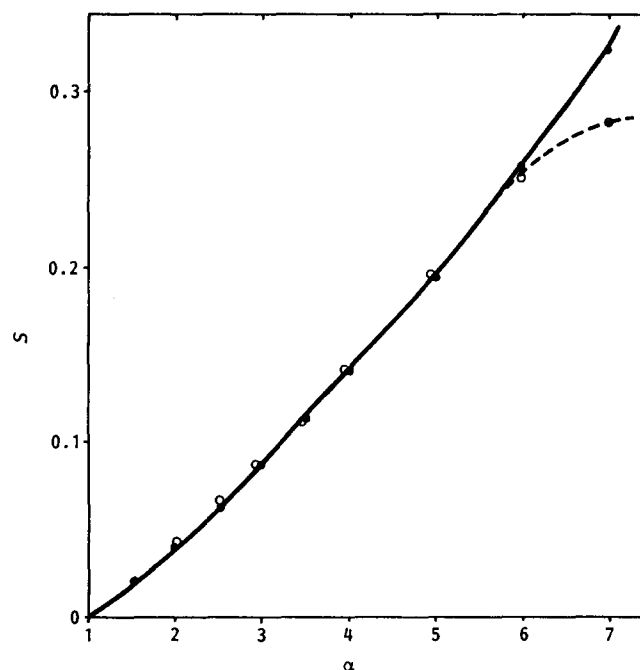


Figure 2 Orientation function S presented in terms of extension ratio α . Full and open circles represent data for the network and dangling chains, respectively. The broken curve represents the deviation of the dangling chain orientation at high α

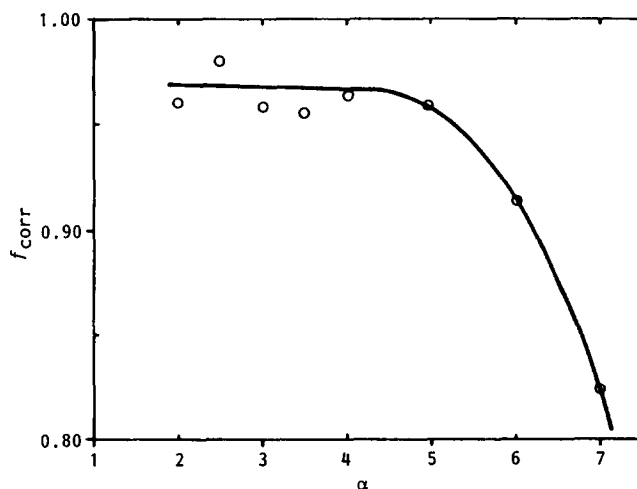


Figure 3 The coupling function presented in terms of extension ratio α . Along the ordinate f_{corr} represents the corrected coupling function according to equation (3)

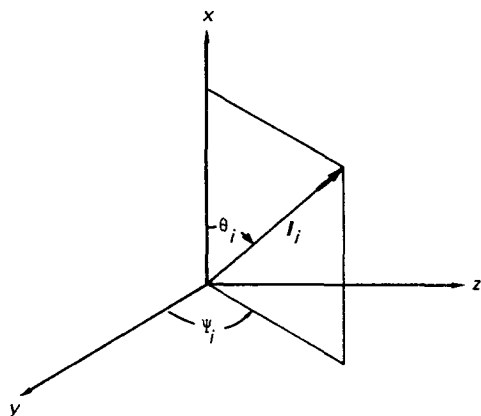


Figure 4 Coordinate system for the i th bond l_i of the freely jointed chain

extensions, probably due to the finite extensibility of network chains which occurs at such high values of α .

The independence of the coupling function f from α has also been observed recently for short flexible probes (9,10-di-n-alkylantracene) dissolved in similar networks⁵. The magnitude of the coupling function was less than the presently reported values, however, for the short probes, and varied between 0.4 and 0.7 depending on the length of the probes. On the other hand, orientation measurements⁶ on rigid-rod probes dissolved in similar networks showed that the coupling function f varies inversely with probe length and depends strongly on α .

DIMENSIONS OF THE DANGLING CHAIN IN THE DEFORMED NETWORK

According to the equilibrium molecular theory of amorphous elastomeric networks^{7,8}, the stress originates from the deformation of chains that are connected to the network structure at both ends. As a result, the free and the dangling chains do not contribute to the macroscopically observed stress. Consequently the overall dimensions of such chains in the deformed network in equilibrium are expected to be isotropic. This long-held view has been shown to be true only recently by neutron scattering experiments⁹ performed on poly(dimethylsiloxane) (PDMS) networks containing free chains. Segmental orientation measurements performed on the same samples by deuterium n.m.r.¹⁰ have shown, on the other hand, that the segments of the free chain are orientationally coupled strongly to their local environments while their overall dimensions were isotropic, as mentioned above.

In this section we show, by the use of a freely jointed chain model, that a free or a dangling chain may indeed exhibit a strong local orientational coupling to its environment with negligible change in its overall dimensions.

The theory of segmental orientation in real networks has been developed recently³ and applied to segmental orientation in *cis*-1,4-polyisoprene networks⁴. It is seen that the constrained-junction model of rubber elasticity theory gives a satisfactory quantitative description of the orientation phenomenon. In the present paper we depart from this model adopted in the two references cited above and describe orientation behaviour in terms of the affine network model. The latter suffices for a qualitative

description of dangling chain orientation addressed in the present study.

The molecular deformation tensor for network chains in an affine network in uniaxial extension is³:

$$\Lambda^2 = \begin{bmatrix} \alpha^2 & 0 & 0 \\ 0 & \alpha^{-1} & 0 \\ 0 & 0 & \alpha^{-1} \end{bmatrix} \quad (4)$$

The segmental orientation function for freely jointed, affinely deforming Gaussian network chains is^{3,5}:

$$S = (1/5n)(\alpha^2 - \alpha^{-1}) \quad (5)$$

where n is the number of Kuhn segments in the network chain. It should be noted that the n^{-1} dependence of the front factor in equation (5) does not result from the affine deformation assumption but is a property of sufficiently long network chains in general³.

In the following we derive an expression for the molecular deformation tensor for the dangling chains and compare it with the one for network chains, given by equation (4).

The i th bond, l_i , of the dangling chain is shown in Figure 4. The coordinate system $Oxyz$ is the laboratory-fixed system. Stretching is along the x direction. θ_i and ψ_i denote the polar and the azimuthal angles of the bond l_i . The vector l_i may be expressed as:

$$l_i = l[(\cos \theta_i)\mathbf{i} + (\sin \theta_i \cos \psi_i)\mathbf{j} + (\sin \theta_i \sin \psi_i)\mathbf{k}] \quad (6)$$

where l is the length of the bond, assumed to be the same for each bond, and \mathbf{i} , \mathbf{j} and \mathbf{k} are the unit vectors along the x , y and z axes, respectively.

The mean-squared end-to-end length $\langle r^2 \rangle$ of a chain of n bonds, when expressed as the dot product of the chain vector, $\mathbf{r} = \sum_{i=1}^n l_i$, has the form:

$$\begin{aligned} \langle r^2 \rangle &= \langle \mathbf{r} \cdot \mathbf{r} \rangle = \left\langle \sum_{i=1}^n l_i \cdot \sum_{j=1}^n l_j \right\rangle \\ &= l^2 \left[\left(\sum_i \langle \cos^2 \theta_i \rangle + \sum_i \langle \sin^2 \theta_i \cos^2 \psi_i \rangle + \sum_i \langle \sin^2 \theta_i \sin^2 \psi_i \rangle \right) \right. \\ &\quad \left. + \left(\sum_{i \neq j} \langle \cos \theta_i \cos \theta_j \rangle + \sum_{i \neq j} \langle \sin \theta_i \sin \theta_j \cos \psi_i \cos \psi_j \rangle \right) \right. \\ &\quad \left. + \sum_{i \neq j} \langle \sin \theta_i \sin \theta_j \sin \psi_i \sin \psi_j \rangle \right] \quad (7) \end{aligned}$$

The angular brackets in equation (7) denote averaging over all configurations of the chain. For a freely jointed chain, the polar angles are independent of the azimuthal angles. Inasmuch as two different bonds ($i \neq j$) are uncorrelated, the terms in the second parentheses of equation (7) vanish. Furthermore, elongation along the x direction results in transverse isotropy in the yz plane. Hence:

$$\langle \cos^2 \psi_i \rangle = \langle \sin^2 \psi_i \rangle = \frac{1}{2} \quad (8)$$

Summing the remaining terms of equation (7) over the n

bonds results in:

$$\langle r^2 \rangle = nl^2(\langle \cos^2 \theta \rangle + \langle \sin^2 \theta \rangle) \equiv nl^2 \quad (9)$$

showing that the scalar quantity $\langle r^2 \rangle$ is independent of the segmental orientation variable, θ . The components $\langle x^2 \rangle$, $\langle y^2 \rangle$ and $\langle z^2 \rangle$, however, depend on θ . The $\langle x^2 \rangle$ and $\langle y^2 \rangle = \langle z^2 \rangle$ terms from (9) are:

$$\begin{aligned} \langle x^2 \rangle &= nl^2 \langle \cos^2 \theta \rangle \\ \langle y^2 \rangle &= \langle z^2 \rangle = nl^2 \langle \sin^2 \theta \rangle / 2 \end{aligned} \quad (10)$$

It is worth noting that a similar conclusion would be reached for the radius of gyration of dangling chains R_G , i.e. $\langle R_G^2 \rangle$ is independent of segmental orientation but $\langle R_{G,x}^2 \rangle$, $\langle R_{G,y}^2 \rangle$ and $\langle R_{G,z}^2 \rangle$ depend on θ . For the latter the dependence will be weaker than that for the components $\langle x^2 \rangle$, $\langle y^2 \rangle$ and $\langle z^2 \rangle$.

Dividing equations (10) by $\langle x^2 \rangle_0 = \langle y^2 \rangle_0 = \langle z^2 \rangle_0 = nl^2/3$ and using the definition of the orientation function for the dangling chains, equations (10) may be presented as the components of the molecular deformation tensor, Λ_d^2 , for the dangling chains:

$$\begin{aligned} \Lambda_d^2 &= \begin{bmatrix} 1+2S_d & 0 & 0 \\ 0 & 1-S_d & 0 \\ 0 & 0 & 1-S_d \end{bmatrix} \\ &= \begin{bmatrix} 1+2fS & 0 & 0 \\ 0 & 1-fS & 0 \\ 0 & 0 & 1-fS \end{bmatrix} \end{aligned} \quad (11)$$

Inasmuch as S_d is of the order of n^{-1} , equation (11) leads to the conclusion that molecular deformation for dangling chains is negligible when compared to the deformation of the network chains, in the limit of large n .

In real chains, where the different bonds are correlated, $\langle x^2 \rangle$ may be expected to be larger. However, deviations from the freely jointed chain behaviour are not expected to be large for sufficiently long chains. This follows from the fact that a sufficiently flexible chain may be subdivided into sequences of bonds where each sequence is uncorrelated with the neighbouring sequences.

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