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Experimental Evidence for a Negative Orientational Order Parameter in a Uniaxially Compressed Poly(dimethylsiloxane) Network

C. Lorthioir,[†] B. Deloche,*[,†] and J. Courtieu[‡]

Laboratoire de Physique des Solides (CNRS-UMR 8502) and
Laboratoire de Chimie Structurale Organique
(CNRS-UPRESA 8074), Université Paris-Sud,
91405 Orsay, France

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Introduction. Uniaxial fluids such as liquid crystals, liquid crystal polymers, polymers under constraint, etc., have been widely studied using NMR. Indeed, this approach is very sensitive to the symmetry of molecular motions and gives access to the so-called orientational order parameter S, which describes the anisotropy of collective fluctuations around the uniaxial symmetry axis of the system. Such NMR investigations are very useful in liquid crystals for characterizing the breaking of symmetry at phase transitions[1] as well as in polymers in regard to the viscoelastic or elastic properties.[2] However, the question of the sign of S is rarely evoked and difficult to solve experimentally. The sign of S is determined by the direction of molecular fluctuations relative to the symmetry axis, which allows one to deduce the average orientation and conformation of the molecules. Such data are then relevant in the study of the macroscopic properties of the considered materials. Obviously, the question of the S sign is meaningless when the degree of order is high ($|S| > 0.5$) as in a nematic mesophase, S being inherently positive. On the other hand, the question remains opened and relevant for systems of low order ($|S| < 10^{-2}$) such as molten polymers under constraint. Experimentally, a direct and unambiguous determination of the sign of S from a single NMR spectrum would be very useful.

NMR Background. The background of deuterium NMR (D NMR) and carbon NMR (^{13}C NMR) in anisotropic fluids is detailed in various references.[3−8] The basic NMR approach to measure a low degree of order S with a high sensitivity consists of observing how strong nuclear interactions are time-averaged by rapid anisotropic molecular motions. The nature of these interactions depends on the observed nucleus. The interactions to consider in D NMR are mainly restricted to the tensorial quadrupolar coupling between a deuteron and the electric environment of the C−D bond whereas in ^{13}C NMR they are scalar *and* tensorial spin−spin couplings ^{13}C−H between the carbon nucleus and protons in the direct vicinity.

Because of the anisotropy of the molecular fluctuations in uniaxial fluids, these tensorial couplings are partially time-averaged along the direction of the macroscopic symmetry axis **n**. These residual interactions are directly proportional to the degree of orientational order S:

$$S = \overline{P_2(\cos\theta(t))} \qquad (1)$$

where $\theta(t)$ in the second Legendre polynomial is the instantaneous angle between the C−D or ^{13}C−H bond relative to the **n** axis.

The total spin−spin coupling interactions $^1T_{\mathrm{CH}}$ (including the scalar $J_{\mathrm{CH}}^{\mathrm{iso}}$ and the dipolar D_{CH} contributions) and the residual quadrupolar interaction Δ_{CD} may be expressed in frequency units as

$$^1T_{\mathrm{CH}} = J_{\mathrm{CH}}^{\mathrm{iso}} + 2D_{\mathrm{CH}} = J_{\mathrm{CH}}^{\mathrm{iso}} + 2\nu_{\mathrm{d}} S P_2(\cos\Omega) \qquad (2)$$

and

$$\Delta_{\mathrm{CD}} = \frac{3}{2}\nu_{\mathrm{q}} S P_2(\cos\Omega) \qquad (3)$$

ν_{d} and ν_{q} are the static dipolar and quadrupolar coupling constants ($\nu_{\mathrm{d}} \sim -20$ kHz, $\nu_{\mathrm{q}} \sim 200$ kHz). ν_{d} is given by

$$\nu_{\mathrm{d}} = -\frac{\mu_0}{4\pi}\frac{\hbar}{2\pi}\frac{\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}}{{r_{\mathrm{CH}}}^3} \qquad (4)$$

where μ_0 is the vacuum permeability ($4\pi \times 10^{-7}$ H m^{-1}), γ_{C} and γ_{H} are the gyromagnetic ratios of carbon 13 and hydrogen nuclei, and r_{CH} is the distance between both nuclei. In both expressions 2 and 3 Ω denotes the angle between the macroscopic symmetry axis **n** and the NMR magnetic field $\mathbf{B}_0$. The overbar in eq 1 holds for a time average over molecular motions faster than the characteristic NMR time ${\nu_{\mathrm{q}}}^{-1}$ or ${\nu_{\mathrm{d}}}^{-1}$. It is clear that, due to the presence of the constant term $J_{\mathrm{CH}}^{\mathrm{iso}}$ (known to be positive) in eq 2, the sign of S may be determined with ^{13}C NMR, contrary to D NMR. In practice, this determination is easy if both terms in eq 2 are not too different in magnitude.

Here we apply the ^{13}C NMR method for a complete determination (sign and magnitude) of the order S induced in a uniaxially constrained polymer network. For clarity, we also include the results obtained via D NMR on the *same* sample. To our knowledge, this is the first time that the S sign is determined unambiguously in a polymeric system from a single NMR spectrum.[9]

Experimental Section. The experiments were performed on a tetrafunctional poly(dimethylsiloxane) (PDMS, $[\mathrm{O{-}Si(CH_3)_2}]_N$) network, containing about 20% of perdeuterated chains. The end-linking reaction and the labeling procedure are outlined in details in ref 10. The degree of polymerization for deuterated and unlabeled subchains is the same ($M_{\mathrm{n}} = 10\,500$ for deuterated chains).

^{13}C and D NMR measurements were performed without proton decoupling on a Bruker AM-400 spectrometer at room temperature. The problem of the S sign was addressed for both uniaxially elongated and compressed polymer networks. Stretching and compression were performed as described earlier.[11,12] The elongation was carried out on a rectangular strip ($20 \times 4 \times 1$ mm^3) along the NMR field $\mathbf{B}_0$ ($\Omega = 0°$). For compression experiments, a cylindrical sample (thickness 1 mm, diameter 4 mm) squeezed between two glass jaws was used, the constraint axis being perpendicular to $\mathbf{B}_0$ ($\Omega = 90°$). The sample deformation was controlled before and after each NMR experiment by means of a

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[†] Laboratoire de Physique des Solides.
[‡] Laboratoire de Chimie Structurale Organique.

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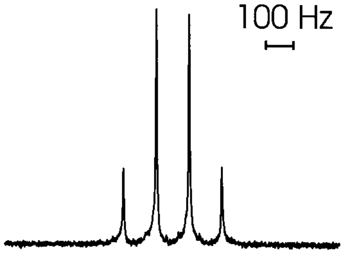

Figure 1. ${}^{13}C$ NMR spectrum of a PDMS melt (average molecular weight of 10 500 g mol^{-1}).

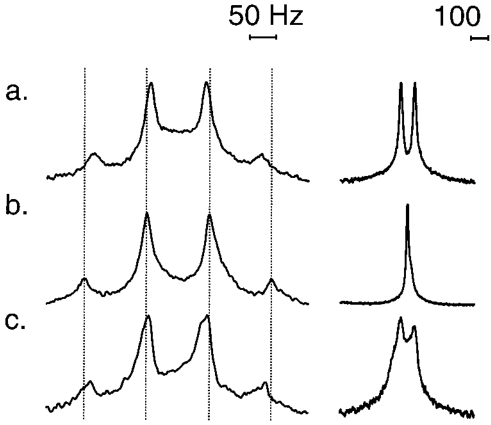

Figure 2. ${}^{13}C$ and D NMR spectra of the PDMS network: (a) in the elongated ($\lambda = 1.46$, $\Omega = 0°$), (b) in the relaxed ($\lambda = 1$), and (c) in the compressed ($\lambda = 0.38$, $\Omega = 90°$) states.

micrometer mounted on a microscope stage. The deformation ratio λ is measured with an accuracy of about 0.2%.

Results and Discussion. Figure 1 shows the ${}^{13}C$ NMR spectrum obtained with a PDMS melt of the same molecular weight as the network chains. As expected for a CH_3 group, the spectrum consists of a quartet centered around the resonance frequency, the respective intensities of the components being in the ratio 1:3:3:1. In such a melt, the ${}^{13}C-H$ reorientations are isotropic on the characteristic time scale ν_d^{-1} ($\nu_d \sim -22.7$ kHz for a methyl group) so that the coupling constant ${}^{1}T_{CH}$ measured on the quartet corresponds to J_{CH}^{iso} only. The observed value, +119 Hz, will be used as a reference for J_{CH}^{iso} in the following.

Figure 2 reports the ${}^{13}C$ and D NMR spectra obtained on a relaxed ($\lambda = 1$), elongated ($\lambda = 1.46$), and compressed ($\lambda = 0.38$) PDMS network. For $\lambda = 1$, the spectral characteristics are similar to those in the melt, i.e., ${}^{1}T_{CH} = J_{CH}^{iso}$ and $\Delta_{CD} = 0$. The observed change of the coupling constant ${}^{1}T_{CH}$ on the ${}^{13}C$ spectra for $\lambda \neq 1$, as well as the doublet structure ($\Delta_{CD} \neq 0$) on the D spectra, shows that the deformed network chain segments undergo anisotropic motions. Previous D NMR investigations on similar PDMS networks have proved that these motions are uniaxial fluctuations around the direction of the applied constraint.[11,13] Then the change of ${}^{1}T_{CH}$ as well as the splitting Δ_{CD} gives direct access to the order parameter S (using eq 2 with $\nu_d = -22.7$ kHz for a methyl group or eq 3 with $\nu_q = 131$ kHz for methyl deuterons), denoted by S_C or S_D, respectively. The plot of $|S_C|$ vs $|S_D|$ reported in Figure 3 shows a perfect concordance between the values of these order parameters, although measured on different time scales.[14]

It has also to be noted that the half-height line width $\delta\nu$ of each quartet component (see Figure 2) remains almost unchanged as the constraint is applied: $\delta\nu \sim 37$ Hz for $\lambda = 1$ as well as for $\lambda = 1.46$ or 0.38. This proves that the distribution of order $P(S)$ remains sufficiently narrow so that a single sign of S is sufficient in the description of the segmental dynamics within the deformed network.

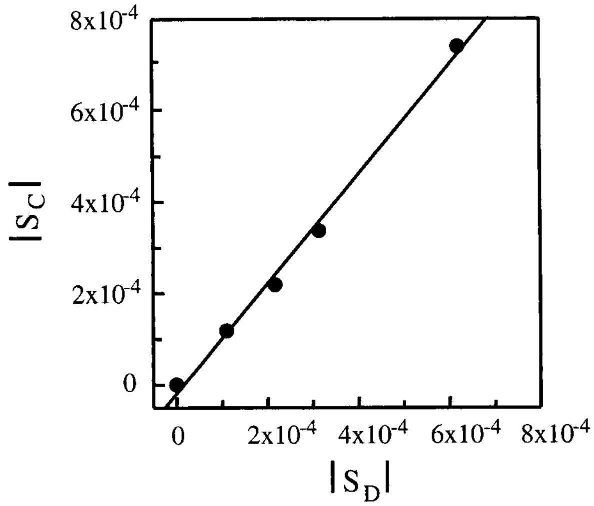

Figure 3. Plot of the absolute value of the orientational order parameter, $|S_C|$ (deduced from ${}^{13}C$ NMR measurements), vs $|S_D|$ (deduced from D NMR). The solid line corresponds to the linear fit of the data.

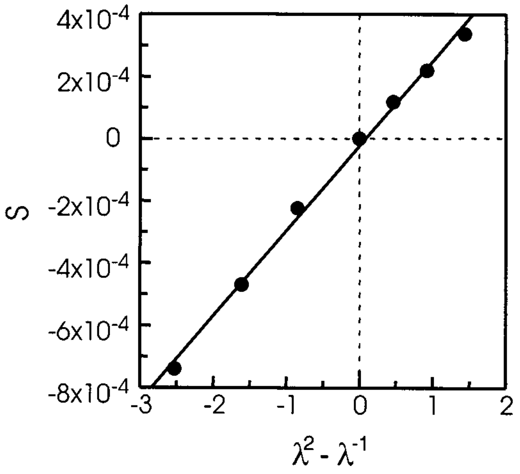

Figure 4. Order parameter S (obtained from ${}^{13}C$ NMR measurements) vs the strain function $\lambda^2 - \lambda^{-1}$, the deformation ratio λ varying between 0.38 and 1.46. The solid line represents the linear fit of the data.

The variation of S (deduced from ${}^{1}T_{CH}$ measurements and eq 2) with the strain function $\lambda^2 - \lambda^{-1}$ for both kinds of deformation is shown in Figure 4. In elongated networks (${}^{1}T_{CH} < J_{CH}^{iso}$, combined with $P_2(\cos \Omega) = 1$), the chain segments exhibit collective fluctuations which are preferentially parallel to the strain axis (i.e., $S > 0$). On the other hand, in compressed networks (${}^{1}T_{CH} < J_{CH}^{iso}$, combined with $P_2(\cos \Omega) = -0.5$), the fluctuations are rather normal to the strain axis (i.e., $S < 0$). It has to be emphasized that the geometry of experiments under compression ($\Omega = 90°$) implies negative values of $({}^{1}T_{CH} - J_{CH}^{iso}) = 2D_{CH}$ and also a weaker sensitivity on λ.

In both compressed and stretched networks, the direction of the applied constraint remains a symmetry axis for the local dynamics. Besides, the λ dependence of S is continuous and linear, even around $\lambda = 1$ (see

Figure 4). In particular, the same slope is observed for both regimes $\lambda < 1$ and $\lambda > 1$. These results mean that the situations of uniaxially compressed and elongated networks are equivalent physically: in each case, short-range orientational correlations between chain segments take place and may be described by the effect of a molecular field parallel to the direction of the applied constraint.[13,15] Under these conditions, the change of the sign of the segmental order may suggest a progressive transition from an average prolate chain conformation (already observed in neutron scattering experiments[16]) to an oblate one.

Contrary to previous D NMR experiments performed on compressed networks,[11,12] a negative sign of the order S is clearly evidenced in this ^{13}C NMR work: this result is a priori not obvious since compression does not imply here bidimensional confinement of polymer chains (sample thickness = 0.6 mm, nonperturbed chain radius of gyration $R_g \approx 57$ Å) as it is the case for polymer nanofilms recently studied by D NMR.[17] Furthermore, the uniaxial local dynamics and the negative sign of S in compressed networks have to be combined with the presence of cross-links, which fixes the averaged positions of chain extremities. This point is also surprising, especially for high λ, since the observed dynamic uniaxiality requires complete reorientational motions of the chain (or subchain) segments around the constraint direction on the NMR time scale.

Finally, the present study demonstrates the possibilities to determine directly both the absolute value and the sign of order parameters S, as weak as 10^{-4}, using ^{13}C NMR via spin−spin coupling measurements. Extensions of this method for investigating the S sign in other confined polymer systems, such as microphase-separated block copolymers, are currently being developed.

References and Notes

(1) Doane, J. W. In *Magnetic Resonance of Liquid Crystals Phase Transitions*; Owens, F. J., Poole, C. J., Farach, H. A., Eds.; Academic Press: London, 1979.

(2) Deloche, B.; Samulski, E. T. *Macromolecules* **1988**, *21*, 3107−3111.

(3) Dong, R. Y. In *Nuclear Magnetic Resonance of Liquid Crystals*; Springer-Verlag: New York, 1994.

(4) Charvolin, J.; Hendrikx, Y. In *Nuclear Magnetic Resonance of Liquid Crystals*; Emsley, J. W., Ed.; D. Reidel Publishing Company: Dordrecht, 1985; p 449.

(5) Samulski, E. T. *Polymer* **1985**, *26*, 177−189.

(6) Deloche, B.; Sotta, P. In *Spectroscopy of Rubbery Materials*; Litvinov, V. M., Ed.; Rapra Technology Ltd: Shrewsbury, to be published.

(7) Pines, A.; Chang, J. J. *Phys. Rev. A* **1974**, *10*, 946−949.

(8) Emsley, J. W.; Lindon, J. C. In *NMR Spectroscopy Using Liquid Crystal Solvents*; Pergamon Press: Oxford, 1975; Chapter 2.

(9) The relationship between S and the degree of order along the chain, at the level of the unit or statistical chain segment, is difficult to establish and model-dependent.

(10) Beltzung, M.; Picot, C.; Herz, J. *Macromolecules* **1984**, *17*, 663−669.

(11) Deloche, B.; Beltzung, M.; Herz, J. *J. Phys., Lett.* **1982**, *43*, 763−769.

(12) McLoughlin, K.; Waldbieser, J. K.; Cohen, C.; Duncan, T. M. *Macromolecules* **1997**, *30*, 1044−1052.

(13) Sotta, P.; Deloche, B. *Macromolecules* **1990**, *23*, 1999−2007.

(14) The very similar values of $|S_C|$ and $|S_D|$ imply that motions with correlation times between ν_d^{-1} and ν_q^{-1} do not occur within the deformed network.

(15) Depner, M.; Deloche, B.; Sotta, P. *Macromolecules* **1994**, *27*, 5192−5199.

(16) Boué, F.; Farnoux, B.; Bastide, J.; Lapp, A.; Herz, J.; Picot, C. *Europhys. Lett.* **1986**, *1*, 637−645.

(17) Zeghal, M.; Deloche, B.; Albouy, P.-A.; Auroy, P. *Phys. Rev. E* **1997**, *56*, 5603−5614.

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