

Mechanical Properties of Monodomain Side Chain Nematic Elastomers^a

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Introduction and motivation. Liquid crystal elastomers have been the object of growing interest over recent years, because they constitute a new class of materials, combining the elastic properties of conventional elastomers and the orientational properties of liquid crystals. They are obtained by chemically linking liquid crystal polymer chains by means of a crosslinking agent. The mesogenic groups can be either macroscopically disordered (poly-domain sample) or macroscopically ordered (mono-domain sample) in the liquid crystalline state.

In contrast to their equilibrium properties, their dynamic properties are much less understood. Recently it has been suggested that there is a separation of time scales by several orders of magnitudes between the director relaxation and the network relaxation (1). Here we demonstrate experimentally on the same system that this hypothesis does not work and that the concept of soft elasticity (2) does not apply.

Theoretical overview. De Gennes (3) was the first to point out that it is important to introduce new terms in the free energy, coupling the director rotations to the permanent network and to perform the calculation of the shear modulus for $\mathbf{n} \perp \mathbf{v}$ (\perp geometry) and $\mathbf{n} // \mathbf{v}$ ($//$ geometry), where \mathbf{n} and \mathbf{v} are the director and the velocity. He predicts a conventional behavior for G'_{\perp} because of the absence of coupling between the director and the shear, and a lowering of $G'_{//}$ associated with this coupling. The linearized hydrodynamic equations ($\omega = 0$) resulting from this picture have been derived by Brand and Pleiner (4).

Very recently, a viscoelastic theory ($\omega \neq 0$) has been developed by Terentjev and Warner (2). This theory is based on the linear elasticity of a network in its low-frequency limit, and on

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an independent relaxation of the director. The essential part of the description is the separation of time scales. It is assumed that the relaxation time of the director (10^{-2} s) is much greater than the time scale of the network which is of the order of the Rouse time (10^{-6} s). As a result, the complex shear modulus shows the conventional behavior of a rubber with a frequency-independent G' for the perpendicular geometry, and a step for G' and G'' , associated with the relaxation of the director for the parallel geometry. Measuring G as a function of frequency is therefore a direct way of testing the theory. In addition, if the concept of soft elasticity is introduced - shape changes without energy cost - it can be shown that G' goes to zero in the hydrodynamic limit (2).

Experimental. The mono-domain nematic elastomer we investigated was synthesized in the Institut für Makromolekulare Chemie, Freiburg, using the method described in (5). It had 90% of mesogens and 10% of flexible crosslinkers. Its chemical structure is shown in Fig. 1.

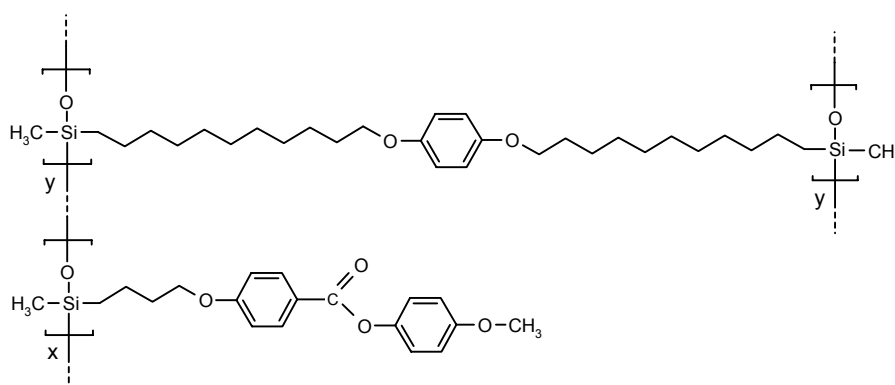


Fig. 1. Chemical structure ($x = 90\%$, $y = 10\%$)

The complex shear modulus $G = G' + iG''$ was measured as a function of frequency and temperature using the piezo-rheometer described previously (6). The principle of this apparatus consists in applying a very small strain ϵ (10^{-4}) to the sample by means of a shear piezoelectric ceramic, and measuring the transmitted stress σ using a second ceramic. The complex shear modulus G of the sample is given by $G = \sigma/\epsilon$. Due to the planar orientation of the director within the film, it was possible to conduct experiments applying the shear parallel or perpendicular to the director and to determine $G_{//}$ and G_{\perp} . The sample was $\sim 380 \mu\text{m}$ thick, and had a surface area of $\sim 0.8 \text{ cm}^2$. It was placed into the cell at room temperature.

Results and discussion. Figure 2 gives the behavior of G' at 1 Hz as a function of temperature when the shear is applied in a direction perpendicular, respectively parallel, to the director. It can be seen that G' is isotropic at high temperature, but becomes anisotropic when the temperature is reduced. The increase of $G'_{//}$ and G'_{\perp} for the lower temperatures, is an

effect associated with the dynamics of the glass transition. The anisotropy of G' , which appears around T_{NI} (T_{NI} was determined by DSC), comes from a lowering of $G'_{//}$. Clearly, $G'_{//}$ is not zero, in contrast to ‘soft elasticity’, and is of the same order of magnitude as G'_{\perp} , in contrast to ‘semi-soft elasticity’. A similar anisotropy was also observed in ref. 1 but interpreted as the signature of dynamic soft elasticity.

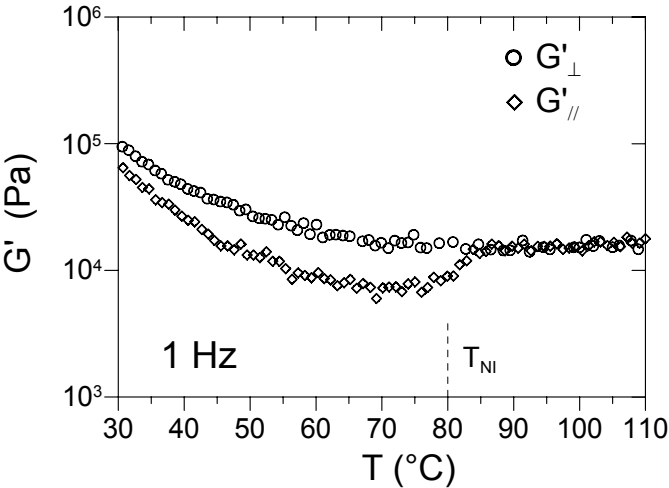


Fig. 2. Behavior of G' as a function of temperature.

We shall now consider the behavior of the shear modulus as a function of frequency. As already explained above, experiments as a function of frequency are the crucial test to determine whether the time scales are separated or not. We shall examine the behavior in the

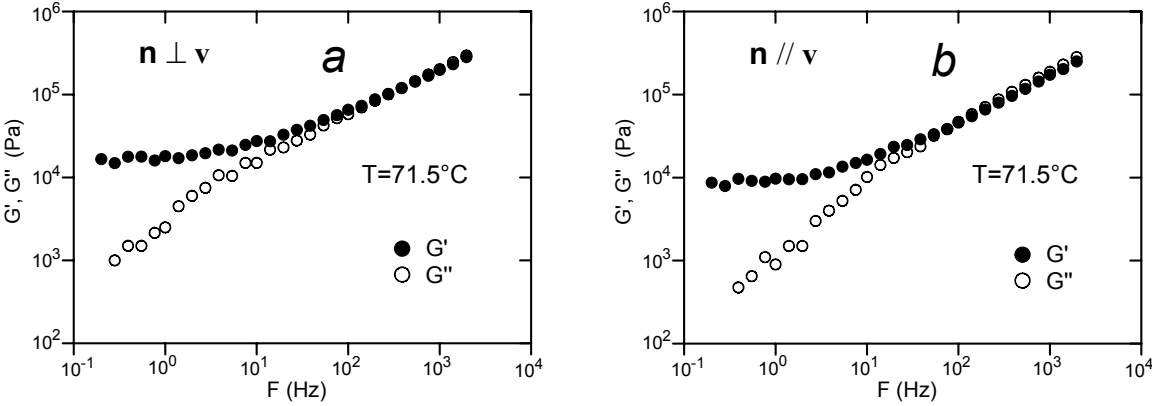


Fig. 3. Frequency variation of G' and G'' .

nematic phase in the temperature range where the mechanical anisotropy is the highest. The results obtained at $T = 71.5^{\circ}\text{C}$ for the perpendicular case are shown in Fig. 3a. It can be seen that the mechanical response of the sample presents two components: one is hydrodynamic

($G = G_0 + i\omega\eta$); the other, which appears at higher frequencies, depends on the frequency and gives rise to a scaling behavior ($G' \sim G'' \sim f^{0.5}$). The key point is that the longest relaxation time of the network is much slower ($\tau \sim 10^{-2}$ s) than the conventional relaxation times of the Rouse modes ($\tau \sim 10^{-6}$ s). This dramatic increase of the relaxation time of the network is in contradiction with the assumption made in refs.1 and 2. It comes from the fact that each monomer bears a bulky mesogenic side group. In this respect, it should be noted that the response of the sample is similar to that observed in the isotropic phase, except for a small variation of the longest relaxation time of the network, which is a simple temperature effect. Fig. 3b shows the results obtained at $T = 71.5^\circ\text{C}$ for the parallel case. Clearly, the behavior is very similar to that for the perpendicular case. The step predicted by the Terentjev-Warner theory is not observed, demonstrating that there is no separation of time scales between the director and the network. This suggests that the relaxation time of the director is “embedded” in the particularly slow Rouse times of the network.

Conclusions. To sum up we have demonstrated that the decoupling approximation hypothesized in ref. 2 does not work, and that the measured relaxation time is the slowest relaxation time of the network, as a whole. The ratio $G'_{\perp}/G'_{\parallel}$ is between 2 and 3, clearly showing the non-soft behavior of these systems. Our results are consistent with the hydrodynamic description of nematic elastomers (3, 4).

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