

Reply to Commentary by E.M. Terentjev and M. Warner on: 'Mechanical Properties of Mono-domain Side Chain Nematic Elastomers'

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Abstract. We argue that all dynamic mechanical experiments on sidechain liquid crystalline elastomers performed up to now can be described without invoking the picture of dynamic soft or semi-soft elasticity.

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1 Static aspects

Although our paper [1] did not deal directly with the question of static soft and semi-soft elasticity, there is certainly a connection and the Comment [2] starts with an extended presentation of this matter, which we have to elucidate on. It has already been noticed by de Gennes [3]

that the shear elastic constant C_{44} is renormalized to $\tilde{C}_{44} = C_{44} - D_2^2/4D_1$, if the nematic degree of freedom is eliminated adiabatically. This is nothing special for nematic elastomers, but a rather common feature in thermodynamics, when of two degrees of freedom, coupled by a bilinear term in a (harmonic) free energy, one is elimi-

nated adiabatically (e.g. cf. Chap.2.5.2 in [4] dealing with the flexoelectric coupling in nematics). Really special for nematic elastomers is the notion of 'soft elasticity' [5,6] meaning $\tilde{C}_{44} = 0$, which was later softened into 'semi-soft elasticity', where \tilde{C}_{44} is not exactly zero, but small due to various kinds of 'imperfections' (cf. Chaps. 7.4-7.6 in [6]). The two concepts of renormalized and semi-soft elastic constants have clearly to be distinguished.

The plateau in Fig.1 of [2], called soft in [2], is associated with a nonlinear effect and does not prove that $\tilde{C}_{44} = 0$. Only the initial slope of the stress-strain curve can be related to the linear response behavior intrinsically assumed for linear elasticity. At large extensions, that is far beyond the linear response regime, where the director is parallel, the elastic modulus has again a finite value comparable to that of the initial slope of the stress-strain curve. In between there is a transition to a heterogeneous texture. The associated plateau does not imply that \tilde{C}_{44} is zero in the two homogeneous regions above and below the plateau, in the same way as the flat part of a $V(T)$ (volume vs. temperature) plot at the liquid to gas transition does not mean that the thermal expansion coefficient is zero in the liquid or in the gas state. A direct test of the soft elasticity concept, i.e. checking whether \tilde{C}_{44} is zero or not in a monodomain sample, consists in measuring the shear rigidity modulus in the linear regime for a suitable geometry.

The symmetry arguments of Golubovic and Lubensky [7] are not applicable, since they require a spontaneous breaking of rotational symmetry due to a sponta-

neous shape anisotropy at the isotropic to nematic phase transition [8]. At this transition however, real side chain elastomers condense into a multi-domain structure without a shape change, if untreated. Only after stretching single domain elastomers are obtained. Then, of course, the shape anisotropy is not spontaneous, in particular for systems that are cross-linked for a second time in the stretched state. Like in ordinary anisotropic solids, there is no symmetry reason for the (shear) modulus to vanish.

2 Dynamic aspects

Now we turn to the discussion of the macroscopic dynamic behavior of nematic elastomers, the description of which has been pioneered in refs. [3,9]. In the following we address some detailed points raised in [2], dealing with the validity of the measurements, dynamic soft elasticity, the power-law scaling of the dynamic moduli G' and G'' , and the possible influence of chemistry. They are discussed roughly in the sequence they are coming up in [2].

1) First we briefly address the issues of the time we have to wait to reach true equilibrium, and of the smallest frequency studied. Both questions also apply to the Cambridge work since the smallest frequency studied in refs. [10–12] is 0.1 Hz. For our measurements equilibrium is achieved when G' becomes frequency independent and concomitantly the phase angle ϕ becomes zero. The lowest frequency studied in [1] is 10^{-1} Hz. This frequency is low enough to obtain true equilibrium in the isotropic phase and for temperatures around the N-I transition, as Figs. 8-10 of [1] show. Fig. 1 of this reply confirms this, by

extending the G' data of Figure 9b down to 0.02 Hz. One should keep in mind that stress relaxation experiments, which are compared in [2] to frequency-dependent oscillatory measurements, have their own experimental problems.

2) In the hydrodynamic regime, the storage modulus G'_{\parallel} , for the (parallel) geometry with the director in the shear plane, is related to \tilde{C}_{44} , while for the geometry with the director *not* in the shear plane, G'_{\perp} comes with C_{44} . Thus, the ratio $G'_{\perp}/G'_{\parallel}$ is larger than one for any nematic side chain elastomer. If dynamic ‘soft or semi-soft elasticity’ [6, 10–13] would apply, this ratio would be infinity or rather very large. However, experimentally we demonstrated that $G'_{\perp}/G'_{\parallel} \sim 2 \dots 3$ for samples 1 and 2. Note, that sample 1 is similar to the LC elastomer, for which the authors of the preceding comment [2] have claimed dynamic semi-soft elasticity. Sample 2 differs from sample 1 by the nature of the crosslinkers, leading to a higher shear rigidity modulus (10^5 Pa versus 10^4 Pa in the isotropic phase). Since the two samples behave the same way entering the nematic phase, the decrease of G'_{\parallel} compared to G'_{\perp} is due to the renormalisation of C_{44} , but not due to semi-softness or softness. This conclusion is also supported by the behavior of the polydomain sample (sample 5) which also shows a small dip of G' around the N-I transition, stemming from the domains that are sheared in a direction parallel to the director.

In contrast to what is claimed in [2], we have never stated that the reduction in C_{44} is a consequence of interacting bulky side groups. The interacting bulky side

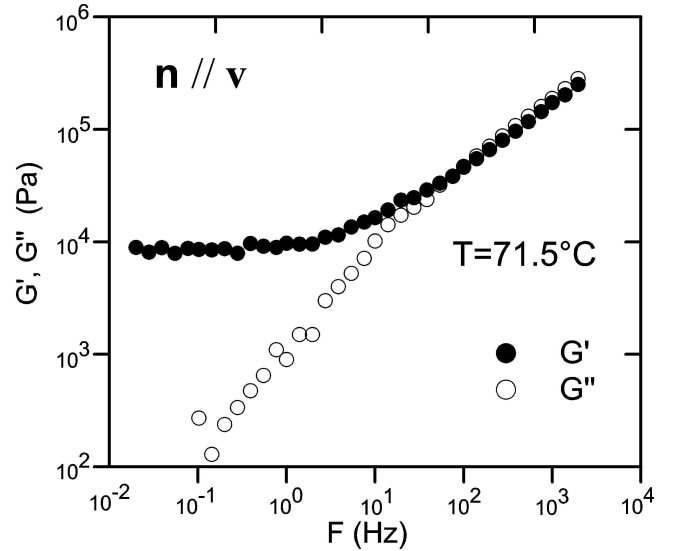


Fig. 1. G' and G'' from fig.9b of [1] are shown for an extended frequency range down to frequencies F of 0.02 Hz.

groups have been discussed in connection with an effective Rouse behavior in [1].

3) Next we discuss the question of the time scales associated with the director and the network. The characteristic time scale for the Rouse-like modes is given by $G' = G''$. We emphasize that the point of intersection is not arbitrary. It gives the value for the time scale of the slowest Rouse mode τ_R . We refer the interested reader to the book of Ferry [14] that includes an extension of the Rouse model to elastomers by Mooney. τ_R is given by:

$$\tau_R = \frac{\xi N_c^2 b^2}{3\Pi^2 k_B T} \quad (1)$$

where ξ is the monomeric friction coefficient, N_c the number of Rouse sequences between two crosslinking points, and b the length of a sequence. The theory of Terentjev and Warner (TW) is based on the separation of time scales between the director and the network with $\tau_n \gg \tau_R$, where τ_n is the relaxation time of the director [10, 13].

This decoupling approximation was used by the Cambridge group to analyse their data, in particular those associated with the sample prepared in the same way as sample 1 [10]. In their commentary, the authors change their point of view and now claim that $\tau_n \ll \tau_R$ for the same sample as before. To obtain this result they have analysed the low frequency part of the master curve given by Fig. 2b in [2] and deduced that τ_R is in between 64 s (assuming $G'' \sim \omega^{0.65}$) and 440 s (assuming $G'' \sim \omega$). By comparing these values to the τ_n value, which they take to be $\sim 10^{-2}$ s, they concluded that τ_R is vastly greater than τ_n . However, τ_R has been evaluated at $T = 22^\circ\text{C}$ (the reference temperature of the master curve) and τ_n at $T \sim 77^\circ\text{C}$. If the temperature dependence of τ_n given in [15] is taken into account, one finds $\tau_n \sim 200$ s, that is of the same order of magnitude as τ_R . So, it is clear that τ_n can be neither $\gg \tau_R$ nor $\ll \tau_R$. τ_n is of the order of τ_R , as we have stated in [1]. It should be noted that eq.1 of [2] is valid only if τ_n is longer than τ_R .

4) We examine now the scaling behavior observed for G' and G'' . Fig. 2b of [2] shows that the viscoelastic part of G' and G'' is characterized by an exponent $n \sim 0.65$, whereas we find $n \sim 0.5$. The authors of [2] indicate that $n \sim 0.65$ is not surprising given that values of n varying from 0.44 to 0.75 have already been reported for side chain nematic elastomers. In fact, these values have been obtained for side chain nematic polymers but not for elastomers, as claimed in [2]. For side chain nematic elastomers we have always found for the exponent n the value $n \sim 0.5$ (see section 6.3 of [1]).

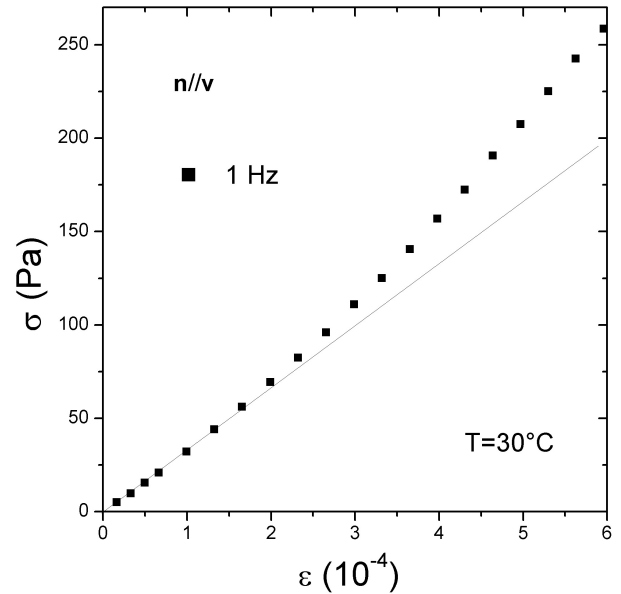


Fig. 2. A stress-strain curve is shown for 1 Hz at $T = 30^\circ\text{C}$. The solid line indicates the result expected for linear response.

In this connection there appears to be an open problem with Fig.2b of [2]. In the linear response regime the value $n = 0.65$ is not compatible with the observation $G' = G''$ in Fig.2b. $G' = G''$ leads to $n = 0.5$. It should be noted that the measurements of the Cambridge group were taken with a strain $\epsilon \sim 2 \cdot 10^{-2}$ [10], whereas ours were taken with $\epsilon \sim 10^{-4}$. Our measurements show that $G' = G''$ and $n = 0.5$, which is the behavior expected in the linear response regime. Fig.2 shows a typical example of the variation of the stress σ as a function of the strain ϵ . It can be seen that σ is proportional to ϵ only for ϵ smaller than $\sim 3 \cdot 10^{-4}$. This definitely shows that the measurements of the Cambridge group are not in the linear response regime, in contrast to what is claimed in [10,12], and can therefore not be interpreted in the framework of linear response theory as it has been done in [10,12]. In this

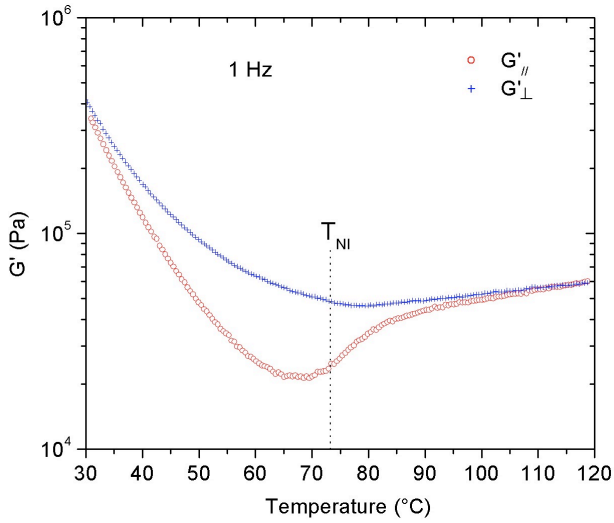


Fig. 3. Temperature dependence of $G'_{||}$ and G'_{\perp} at 1 Hz around the NI-transition,

connection there appears to be a second problem with Fig. 2b [2], which shows that the low frequency behavior is characterized by $G' = cst$ and $G'' \sim 0.65$, whereas our experiments performed within the same frequency range than those of the Cambridge group show that $G' = cst$ and $G'' \sim \omega$. It should be noted that all the elastomers we have investigated show a hydrodynamic behaviour ($G' = cst$; $G'' \sim \omega$) in the low frequency limit.

5) The last point concerns the chemistry. The authors of [2] indicate that the exponent n depends on delicate aspects of preparation even if exactly the same chemistry were to be used. To address the influence of modifications in the chemistry, we have recently performed measurements on a sample similar to sample 1 of [1], for which the crosslinking process was different with remaining unreacted monomers (swelling degree $q = 4.3$; $T_{ni} = 73^{\circ}C$). Our results show that there is no change in the ratio $G'_{\perp}/G'_{||}$, which is ~ 2.5 at $T \sim 65^{\circ}C$, and the value of

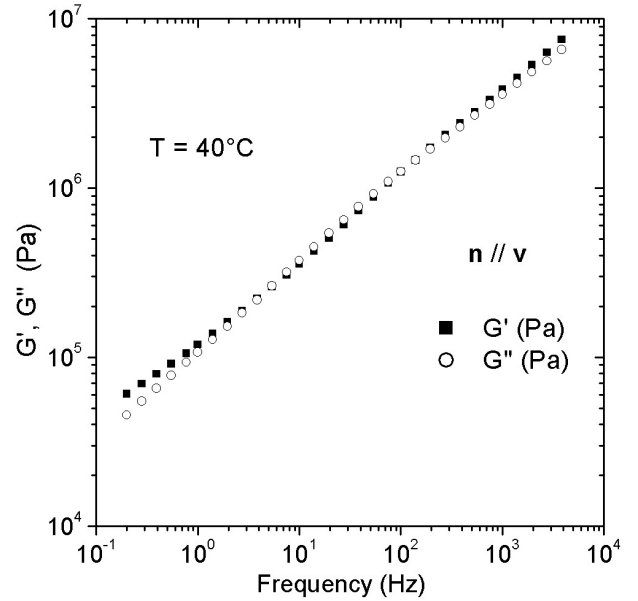


Fig. 4. Frequency variation of G' and G'' at $40^{\circ}C$ for the parallel geometry.

n (~ 0.5). To demonstrate this we present here Figures 3 and 4, which respectively show the temperature dependence of $G'_{||}$ and G'_{\perp} at 1 Hz between $30^{\circ}C$ and $120^{\circ}C$, and the frequency variation of G' and G'' at $40^{\circ}C$ for the parallel geometry. These results demonstrate that modifications in the chemistry do not change our picture - in contrast to what has been suggested in the previous comment [2] - and therefore 'soft elasticity' is not involved.

In contrast to what is stated in [2], the exponent $n \sim 0.5$ is not a direct evidence of soft elasticity. This exponent is, for example, also observed in the isotropic phase of samples exhibiting an isotropic to smectic A phase transition, and in polydomain samples (see section 6.3 in [1]).

To sum up we have argued that all dynamic mechanical experiments performed so far can be described without invoking the concept of dynamic 'soft or semi-soft elastic-

ity'. To explain the dip in G'_{\parallel} in the parallel geometry a macroscopic description [3,9] turns out to be completely sufficient [1]. In particular, the values of $G'_{\perp}/G'_{\parallel}$ and n are, in a first approximation, not, or at most only very weakly, system dependent. A second plateau expected from dynamic soft elasticity [10,13] has not been observed.

Since hydrodynamics is connected to statics, the results presented in [1] show no evidence for static 'soft or semi-soft elasticity', suggesting that there is another possibility to explain the results in Fig.1 of [2].

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