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Nematic Networks: On Thermoelasticity and the Bridging Fraction

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Nematic networks and gels exhibit a number of distinctive traits such as a mechanical critical point[1] and a history-dependent phase diagram.[2,3] These features result from the coupling between the elasticity of the networks and the nematic order. Other special traits are solely due to the effect of the nematic order on the configurations of the liquid crystalline polymers forming the network. In the following we discuss two such effects. Both involve networks of thermotropic main-chain liquid crystalline polymers (LCPs). These consist of mesogenic monomers joined by short flexible spacer chains.[4] The mesogenic monomers are thus incorporated into the backbone of the polymer. The elastic properties of these LCPs in the isotropic and the nematic states differ significantly. These differences give rise to the effects in question. One effect is an *exponential* temperature dependence of the elastic modulus, E, and of the associated force law. In marked distinction, networks of flexible, non-liquid crystalline polymers exhibit a linear T dependence. The second trait concerns the equilibrium bridging fraction, q, in thermotropic elastomers formed by ABA triblock copolymers with a LCP B block. In the nematic state q is expected to be significantly *higher* in comparison to its value in the isotropic case.

For brevity, we limit are discussion to the case of "single-crystal" lamellar mesonetworks (Figure 1)[5,6] obtained from ABA triblock copolymers. Such samples are formed from a lamellar melt which is oriented by shear at a temperature T_i and then quenched to T_q, where T_q is below the glass transition temperature of the A domains. A network is obtained because for some of the B blocks each A block belongs to a different domain, thus giving rise to a bridge (Figure 1). In other cases the two A blocks belong to the same domain, thus creating a loop. We consider the fraction of bridging B blocks, q, in nematic layers of a B melt. The quench is assumed to be rapid, so the bridging fraction of B blocks is frozen at its initial value, i.e., its value at temperature T_i. Since the A domains are, ideally, perfectly rigid, our discussion of the stretching force law and the Young's modulus concerns lamellar mesogels obtained upon swelling of the dry network by a nematic solvent. We thus avoid the incompressibility constraint which would otherwise prevent simple extension and compression. By limiting our discussion to these situations, we eliminate complications due to nonplanar geometries. The precise form of our results is thus applicable to these special systems. However, the effects described are *general* and are expected to play a role in networks of main-chain LCPs irrespective of geometry and state of swelling.

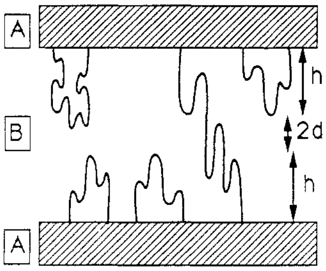

Figure 1. Schematic cross-section of a lamellar mesogel. The two exterior "A" layers (hatched) are glassy. The central "B" layer is nematic and incorporates both loops and bridges of main-chain LCPs with hairpins.

Both effects are due to the modified elastic behavior of LCPs in the nematic state. In this state the chains assume anisotropic, cigar-like shapes which are aligned with their major axis parallel to the nematic field. Their trajectory follows, on average, the nematic field. However, the LCPs can also support "hairpin defects".[7-9] These are abrupt reversals in the trajectory of the chain. Their existence was predicted by de Gennes in 1982[7] and was recently confirmed experimentally.[10] The hairpins determine the size of the LCP along its major axis, $R_\|$, and the deformation behavior of $R_\|$. Their number per chain is $n_0 = (L/l)\exp(-U_h/kT)$, where L is the chain contour length, l is a microscopic length, and U_h is the energy per hairpin. Here "0" refers to the unstretched state of the chain. The chain configuration in the direction of the nematic field may be viewed as a one-dimensional random walk of n_0 steps of average length L/n_0. The average span of the chain in this direction is thus $R_{\|0}^2 \approx L^2/n_0 \approx Ll\exp(U_h/kT)$. Before discussing mesonetworks, we first make some remarks on the elasticity of a single chain. In general, the stretching behavior of $R_\|$ is non-Gaussian since the number of steps of the random walk can change with extension. This leads to a novel Ising elasticity.[11,12] In the following we confine our discussion to weak deformations for which Gaussian extensional behavior, $F_{el}/kT \approx R_\|^2/R_{\|0}^2$, is recovered. This is nevertheless very different from the Gaussian behavior of the LCP in the isotropic state. In the isotropic case the LCP may be viewed as an isotropic random walk consisting of L/ζ steps of length ζ, where ζ is the persistence length. Accordingly, $R_0^2 \approx L\zeta$ and $F_{el}/kT \approx R^2/R_0^2$. The isotropic elasticity of a single chain is thus much stiffer than that of a nematic chain since $R_0^2 = L\zeta \ll R_{0\|}^2 = Ll\exp(U_h/kT)$. Furthermore, ζ is only weakly dependent on temperature, and the Gaussian free energy in the isotropic state is linear in T. In the nematic state F_{el} depends exponentially on T through $R_{\|0}^2$. The corresponding elastic free energy density, f_{el}, is also modified. For flexible isotropic chains $f_{el}/kT = a^{-2}(\mathrm{d}r/\mathrm{d}n)^2$ irrespective of direction, where $r(n)$ is the spatial position of the nth monomer. On the other hand, for LCPs in the nematic state f_{el} due to extension of $R_\|$ is of the form $f_{el}/kT = (al)^{-1}\exp(-U_h/kT)(\mathrm{d}r_\|/\mathrm{d}n)^2$,[12] where $r_\|(n)$ is the position of the nth monomer along the director direction. The exponential temperature dependence of the Young's modulus E, the elastic force law, and f_{el} are of course closely related. The increase in q is due to the weakening of $f_{el}(R_\|)$.

To qualitatively understand the temperature dependence of E it is sufficient to consider a swollen lamellar mesogel in the limit of $q = 1$, where all the chains bridge. In this case the Alexander model[13] is strictly applicable: The chains are uniformly stretched and the concentration of B monomers within the layer is constant. The free energy per chain is accordingly $F_{chain}/kT \approx v_n N^2/\Sigma H + (1/2)H^2/R_{\|0}^2$, where Σ is the surface area per B chain, v_n is the second virial coefficient in the nematic phase, H is the thickness of the stretched B layer, and T is the

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temperature in the *quenched* state. This may be rewritten as $F_{\mathrm{chain}}/kT \approx [H_{\|0}/H + (1/2)H^2/H_{\|0}^2](H_{\|0}^2/R_{\|0}^2)$, where $H_{\|0} = \upsilon_n^{1/3}N(al/\Sigma)^{1/3}\exp(U_{\mathrm{h}}/3kT)$ is the unstretched height of the B layer. The restoring force due to a deformation is $f = -\partial F_{\mathrm{chain}}/\partial H$, while the associated external pressure is $P_N = -f/\Sigma$. We now deform the gel by stretching. If the height of the nematic layer changes by a factor $1 + \alpha$, $H = H_{\|0}(1 + \alpha)$, then the strain on the gel, accounting for the fact that the A blocks do not deform, is $\alpha/(1 + H_{\mathrm{A}}/H_{\|0})$, where H_{A} is the A layer spacing. Young's modulus is then $E = (1 + H_{\mathrm{A}}/H_{\|0})\,\mathrm{d}P_N/\mathrm{d}\alpha = (1 + H_{\mathrm{A}}/H_{\|0})(kT/\Sigma)(H_{\|0}/R_{\|0}^2)$ or

$$E = (1 + H_{\mathrm{A}}/H_{\|0})(kT/al)\Sigma^{-1}(\upsilon_n al/\Sigma)^{1/3}\exp(-2U_{\mathrm{h}}/kT) \sim kT\exp(-2U_{\mathrm{h}}/3kT) \quad (1)$$

The exponential decrease in the Young's modulus is clear in this expression. Note, however, that there is also some temperature dependence through Σ. This is weaker since it is controlled in part by the isotropic blocks. A more sophisticated self-consistent field (SCF)[14-16] analysis is required to obtain the q dependence of E. However, $E \sim q^{2/3}$ behavior is expected in view of the straightforward correspondence between the isotropic case and the LCP brush.[6]

The second effect, the increase in the bridging fraction q in the nematic melt state, is due to the corresponding weakening of the chain elasticity. Two factors determine q: the difference in free energy between loops and bridges and the mixing entropy of the two species. The free energies of loops and bridges are indistinguishable within the Alexander model. It is thus necessary to invoke SCF theory to obtain the difference between the two. An extensive summary of this calculation is beyond the scope of this Note. The essential ingredients are as follows. Because of symmetry it is possible to formulate the theory for half a layer. The bridging chains are considered as constrained on both ends, while loops are treated as two halves with free ends. The SCF analysis suggests that the B layer consists of three regions[6] (Figure 1): a central region, of thickness $2d$, consisting solely of uniformly stretched bridging chains, and two boundary layers, of thickness h, incorporating both bridges and loops. In the boundary layers the stretching degree varies with the distance from the surface, x. The average elastic free energy per chain at the boundary layer is $F_{\mathrm{b}}/kT = (1 - q)(3/2al)\exp(-U_{\mathrm{h}}/kT)\int_0^h d\eta\, g(\eta)\int_0^\eta E(x,\eta)\,\mathrm{d}x + q(3/2al)\exp(-U_{\mathrm{h}}/kT)\int_0^h E_{\mathrm{b}}(x,h)\,\mathrm{d}x$, where $E_n(x,\eta) = \mathrm{d}x/\mathrm{d}n$ is proportional to the local tension, $kT(3/al)\exp(-U_{\mathrm{h}}/kT)E_n$, in a chain whose end is located at height η and $g(\eta)$ is the height distribution function of ends. Here, T is the temperature before the quench. $E_{\mathrm{b}}(x,h)$ is proportional to the local tension in a bridging chain whose end points are always located at h. The elastic free energy per chain in the central region is $F_{\mathrm{c}}/kT = 3q(H_0 - h)^2/[2(N - N')al\exp(U_{\mathrm{h}}/kT)]$, where $2N$ is the polymerization degree of the B block, N' is the number of monomers in the boundary layer, and $H_0 = Na^3/\Sigma$ is the equilibrium thickness of the layer. By minimizing $F_{\mathrm{b}} + F_{\mathrm{c}}$ subject to the appropriate constraints, one obtains the average elastic free energy per chain $F_{\mathrm{el}}(q)$. In the limit of small q, $F_{\mathrm{el}}/kT = (F_{\mathrm{el}}^0/kT)[1 + (2q/\pi)^4]$. The equilibrium value of q is found by minimizing the total free energy per B chain, $F_{\mathrm{chain}}/kT = F_{\mathrm{el}}(q)/kT + q\ln q + (1 - q)\ln(1 - q)$. For small q we need to solve $4(F_{\mathrm{el}}^0/kT)(2/\pi)^4q^3 + \ln q = 0$. This can be solved numerically and leads to an approximate scaling form[17] $q_{\mathrm{eq}} \sim (kT/F_{\mathrm{el}}^0)^\beta$, with $\beta \approx 1/4$, so that

$$q_{\mathrm{eq}} \approx (R_{\|0}/H_0)^{1/2} \approx (\Sigma^2 l/Na^5)^{1/4}\exp(U_{\mathrm{h}}/4kT) \quad (2)$$

This shows clearly the exponential enhancement of the bridging fraction.

Some of the distinctive properties of nematic networks of main-chain LCPs are thus traceable to the special configurations adopted by LCPs in the nematic state. The Boltzmann factor characterizing the hairpin distribution gives rise to the exponential T dependence of the elastic modulus and related properties. It also results in enhancing the equilibrium bridging fraction in physical networks formed by triblock copolymers with a liquid crystalline middle block. These effects are novel in comparison to the behavior of isotropic networks formed by flexible, non-liquid crystalline polymers. From the perspective of LCP research these features are examples of an exponential T dependence which characterizes many features of main-chain LCPs with hairpins:[7-9,18-22] chain dimensions, the splay elastic constant, the dielectric response, cyclization properties, etc.

Finally, here we have examined briefly the extensional behavior of mesogel networks. In compression, other novel effects are expected. In particular, a tilting transition should occur.[23,24]

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