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Spontaneous Ordering in Polymeric Nematic Liquids and Solids [and Discussion]

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Spontaneous ordering in polymeric nematic liquids and solids†

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Polymers can spontaneously orientationally order when rod-like elements form the main chain or are pendant as side chains from the backbone. There exists strong coupling between chains and nematic order. Thus unlike simple rod liquids where the molecules remain undistorted on ordering, these molecules become elongated or flattened. Shape change is at the heart of polymer properties and new character enters the liquid crystal problem. Characteristic ordering of both main and side chain nematic melts, and the concomitant shape response will be discussed.

Polymer networks (elastomers) exhibit rubber elasticity, that is resistance to macroscopic shape change reflecting the loss of freedom of chains distorted by applied stress. On the other hand spontaneous microscopic shape changes resulting from nematic ordering, bring with them the spontaneous macroscopic shape changes seen in experiments on nematic monodomain elastomers. The anisotropy of chain shape at chemical crosslinking is permanently recorded. Conversely there are stress-nematic effects unknown in simple nematics.

1. Introduction

An important example of self order in polymers is that of nematic order. I discuss the development of nematic order and the profound effect it has on the form of such polymeric materials. Essential in building nematic polymers is the incorporation of rod-like (liquid crystal forming) elements. This can be achieved by linking the rods together to form the backbone of the polymer itself (main chain (MC) polymers), or by linking the rods to a rather flexible backbone as side chains (side chain (SC) polymers). When stiff elements are in both the backbone and side chain, these polymers have been termed 'combined' polymers. The various possibilities, their chemical structures, the resulting physical properties, modelling, applications to nonlinear optics and other uses have been reviewed at length in a book edited by McArdel (1989). A more recent review with many references is that of Warner (1993).

Self ordering and related responses to external fields lead to many uses for polymer liquid crystals. For instance the nematic ordering and subsequent poling of side chain rods in SC polymers has been used for NLO media, since polymers produce superior glassy films and the attachment of the rods to the backbone ensures high dye fractions without the phase separation that can result when polymers

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are simply used as a host for conventional dyes. These are useful characteristics, but in this article I discuss the more distinctly polymeric implications of self ordering for form. In conventional polymers the unusual viscoelasticity for example arises because the process (flow) causes chain shape to be modified. The internal entropy associated with the many configurations of chains is reduced because of shape change and the free energy rises. Other classical examples are rubber elasticity and the extension of chains as polymer crystallization proceeds. These three examples are unique to polymers because of the extended molecules and their capacity to react geometrically. In all of these cases macroscopic form is modified by the order that has been imposed. For instance in rubbers the molecular shape change is mirrored in the macroscopic strain. In contrast nematic polymers, even those with a high degree of internal flexibility, have the capacity to self order. Effects such as in the strain of rubbers and in the flow alignment of melts can obtain spontaneously. In confining ourselves to such unusual phenomena we exclude discussion of very rigid nematic polymers, such as the highly rod-like PBLG, which lack the internal degrees of freedom of conventional polymers and are in some sense like very long conventional nematic rods.

We shall discuss the self ordering of MC and SC nematic polymers. Simple models will be given, appropriate to the various different geometrical classes that arise. Complex self ordering is shown to arise in the combined cases where main and side chain nematogens compete for the most favourable nematic direction. The last part of this review addresses nematic elastomers, where self ordering and the concomitant molecular shape changes have their most dramatic consequences for form; strains analogous to those in conventional elastomers but occurring spontaneously.

2. Molecular shape and ordering in nematic melts

Neutron scattering by D'Allest *et al* (1988) from MC nematic polymers shows that chains isotropic in the high-temperature phase become elongated along the nematic director and contracted in the two perpendicular directions. The isotropic–nematic transition is discontinuous, and so too is the change in shape. Such chains are essentially gaussian with one step length l^o characterizing the chain shape in the iso-phase: the radius of gyration is given by $\langle (R^o)^2 \rangle = l^o L$, for chain of length L. In the nematic phase there are two radii of gyration: $\langle (R^o_{\|})^2 \rangle = l^o_{\|}(Q)L$, $\langle (R^o_{\perp})^2 \rangle = l^o_{\perp}(Q)L$ and hence two effective step lengths. Chain shape clearly depends on the nematic order parameter $Q = \langle P_2(\cos\theta) \rangle$ (θ is the angle that the chain locally makes with the mean ordering direction). Often for MC polymers $l_{\|} \gg l_{\perp}$ because the nematic field induces correlations, in excess of those purely from chain stiffness, between adjacent rods along the backbone. This large anisotropy in shape has been observed by D'Allest *et al* (1988), see figure 1. Here the effective steplength $l_{\|}$ parallel to the director increases by a factor of at least 16. We picture this melt phase in figure 2 *a*. Note that in figure 2 *a* the order parameter Q of the backbone is positive. The chain has on average the shape of a prolate spheroid.

Side chain polymers by contrast can have their backbones prolate or oblate, depending on whether the backbone or side chains dominate the nematic ordering. Figure 2 *a* shows two more prolate phases and figure 2 *b* an oblate phase. In general

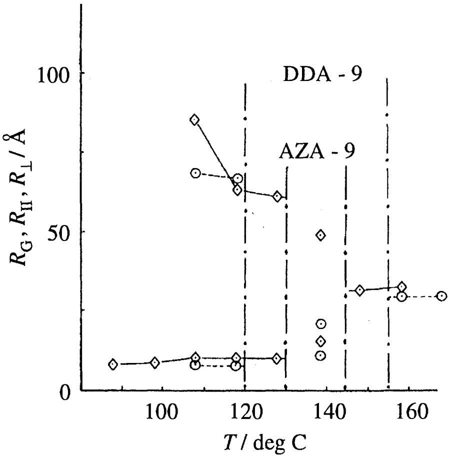
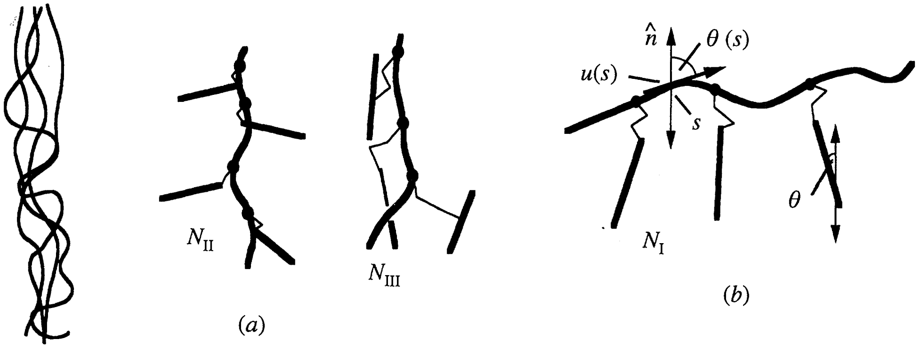


Figure 1. Neutron scattering determination of the shape of a main chain polymer liquid crystal above and below the nematic isotropic phase transition. [Reproduced with permission from D'Allest *et al* (1988).]



(*a*)

(*b*)

Figure 2. Prolate and oblate nematic polymers (*a*) prolate phases: the MC phase shown as a melt of worms, that is where the stiffness along the backbone is considered smoothed out, and the SC phases N_{II} and N_{III}. These are shown as individual chains to illustrate the architecture of stiff teeth attached via spacers to the backbone, itself capable of being stiff. These SC polymers elongate along the ordering direction, the director $\boldsymbol{n}$. Note that the spacers are either bent (naturally, or by the nematic field) or the attachment is perpendicular. (*b*) shows the N_I phase where SC ordering dominates. The spacer is perpendicular and forces the backbone to be oblate, that is to flatten. The local chain direction $\boldsymbol{u}$ at the arc point s and the direction of a SC element make the relevant angles θ with the director. These definitions are appropriate to the other cases also.

chain shape in the nematic phase is not so anisotropic for SC systems as for MCs, see for instance the neutron scattering studies of Kirste & Ohm (1985). This is partly because the backbones involved are mostly more flexible than in MC systems which are stiffened by their rods, and partly because the nematic order, if principally in the side chains, is not so directly coupled to the backbone as in the MC system where it is instrinsic to the backbone.

One can describe main chain polymers as worms of length L with a bend constant ϵ. A worm has a tangent vector $\boldsymbol{u}(s)$, a unit vector needed to specify the local direction of the chain. The probability distribution of chains is then

$$p \sim \exp\left[-\frac{\epsilon}{k_B T}\int_0^L \mathrm{d}s\, \dot{\boldsymbol{u}}(s)^2 + \frac{aQ}{k_B T}\int \mathrm{d}s\, P_2(\cos\theta(s))\right], \tag{2.1}$$

where the dot indicates $\partial/\partial s$, $\theta(s)$ is the angle the chain at arc point s makes with the ordering direction (see figure 2, where it is actually defined for the backbone tangent of a SC polymer), and a is the nematic coupling per unit arc length of chain. This mean field potential is the simplest form that can be chosen that is consistent with the quadrupolar symmetry of a nematic. Much is subsumed in this apparently simple form, for instance both packing effects and soft interactions, the former being athermal entropic influence, the latter giving rise to thermal phenomena. This is discussed at length by Warner (1993) where references to many different approaches are given. Such persistent chains are gaussians if $L > l^o$, where the persistence length, l^o, in for instance the isotropic phase of this model is $l^o = \epsilon/k_B T$. The elongation in $\langle (R^o_{\parallel})^2\rangle$ is thus seen in the growth of $l^o_{\parallel}$. For freely hinged rod models of polymers the growth is by a maximum factor of 3. Although the component rods become aligned and all steps are constrained to be up and down the ordering direction, free hinging allows random changes of direction between steps and therefore no coherence between steps. In contrast the worm chain can be squeezed out to become a rod. The maximum growth factor is N, the degree of polymerization of the chain. In the final stages the growth is via de Gennes (1982) hairpins, the rapid growth of chain dimensions seen by D'Allest *et al.* (1988). Form here is a consequence of bend and nematic potentials acting against the usual randomising of chain conformations found in polymers.

The phase transition in nematic worms is at $k_B T_{NI} = 0.388\sqrt{a\epsilon}$ with order $Q_{NI} = 0.35$ at the transition. This is a universal result, supposedly characteristic of all chains. Of course the various disparate effects subsumed into the nematic potential render this universality invalid, but the model describes the great growth and the interplay between nematic and elastic bend forces. The underlying temperature scale $\sim \sqrt{a\epsilon}$ is quite different from that of the SC part of the problem which is more akin to the Maier–Saupe system, see below.

At the other end of the spectrum of behaviour is that of a freely jointed rod polymer being ordered by nematic interactions. It is a simpler model and in some cases more appropriate, but it cannot lead to the large anisotropy in shape observed by D'Allest *et al.* (1988). The direction θ of a test rod is independent of the neighbouring rods along the chain, clearly not always a useful approximation. It is governed by the distribution

$$p(\theta) \sim \exp\left[\frac{vQ}{k_B T}P_2(\cos\theta)\right]. \tag{2.2}$$

Again the coupling v subsumes the two principal effects discussed above. The problem for each constituent rod of the polymer is the classic Maier–Saupe problem of simple nematics (Maier & Saupe 1958) and has the same universal solution (with the same shortcomings) for the nematic–isotropic transition, $k_B T_{NI} = 0.22v$ with $Q_{NI} = 0.43$. This model was adopted for instance by Abramchuk *et al.* (1987, 1989) in connection with nematic elastomers. It has the attractive simplicity that the chain shape has a simple geometrical relation to the nematic order since $Q = \langle P_2(\cos\theta)\rangle = \langle \frac{3}{2}(\cos\theta)^2 - \frac{1}{2}\rangle$ and $\langle (R^o_{\parallel})^2\rangle = l^o L\langle(\cos\theta)^2\rangle = l^o L(1+2Q)/3$

and $\langle (R_\perp^o)^2\rangle = \frac{1}{2} l^o L \langle(\sin\theta)^2\rangle = l^o L(1-Q)/3$. l^o is now the length of one of the component rods. One sees immediately that the maximum growth between the states $Q=0$ (isotropic melt) and $Q=1$ (perfect nematic order) is a factor of 3. It seems unlikely that freely jointed rod models are relevant to MC polymers with their stiff units in the backbone and with their rapid expansion below T_{NI}. However, they may be of use in describing SC polymers with flexible backbones.

One can visualize SC polymers as worm backbones with rods hinged to them. The probability above can be extended to include the side chain elements and the cross coupling between the backbone and side chains:

$$p \sim \exp\left[-\frac{\epsilon}{k_B T}\int_0^L \mathrm{d}s\, \dot{\boldsymbol{u}}(s)^2 - \frac{U_B}{k_B T}\int \mathrm{d}s\, P_2(\cos\theta(s)) - \frac{U_A}{k_B T} P_2(\cos\theta_A)\right], \quad (2.3)$$

where the potentials felt by rods (A) at angle θ_A and thebackbone (B) are characterized by, respectively,

$$U_A = -x[\chi v_A Q_A + (1-\chi)v_{\mathrm{m}} Q_B], \quad U_B = -[\chi v_{\mathrm{m}} Q_A + (1-\chi) v_B Q_B]. \quad (2.4)$$

The volume fraction of side chain in the polymer is χ. The coupling constants denote rod–rod, v_A, backbone–backbone, v_B, and the mutual, v_{m}, coupling. The order parameters of the two separately ordering parts of the molecule have the appropriate distinguishing subscripts. The SC rods are of length x and the effective, Maier–Saupe like nematic coupling per rod is xv_A, where v_A is a nematic coupling per unit length($xv_A \equiv C$ of the discussion of nematic ordering. Self ordering is now more complex because there are two order parameters, see the original papers Vasilenko *et al* (1985) and Wang & Warner (1987). The review by Warner (1989) in McArdle (1989) gives a fuller qualitative discussion than the sketch below.

Inspection of the potentials show backbone and side chains to be in a nematic field due to its own order and the nematic field of the other species, the latter effectively an external field inducing order. The self fields give the characteristic temperatures $k_B T_B = 0.388(1-\chi)\sqrt{v_B \epsilon}$ of the BB and of the SC, $k_B T_A = 0.22\chi x v_A$, determining which species will order first and force the other to follow in a paranematic fashion. The other can possibly suffer a phase transition at a lower temperature approximately equal to its own characteristic temperature.

The mutual coupling, v_{m}, contains two influences, the backbone-side chain nematic coupling driving the two to be parallel (a positive contribution) and the effect of the hinge. If the hinge tends to orient the side-chain at right angles to the backbone, then its contribution is negative, if the hinge is naturally bent and drives the two to be parallel, the contribution is positive. Wang and Warner (1987) discuss how v_{m} is composed.

Positive v_{m} is straight forward because all three influences drive the back-bone and side chains to be parallel. This is the prolate N_{III} phase shown in figure 2 *a*. Both order parameters Q_A and Q_B are positive. When v_{m} is negative then there is competition between MC and SC ordering. The dominant species adopts a positive order parameter, the other is forced by the hinge to be negative, see figure 2 *b*, where the phase N_{I} has dominant side chains and the backbone is pressed down to a flattened (oblate) form. Conversely in N_{II} (figure 2 *a*) side chains resemble the bristles on a bottle brush with the backbone in a prolate (dominant) phase. As the volume fraction χ of side chains changes, then so does this balance. High

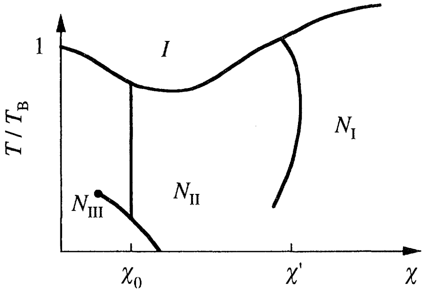


Figure 3. Temperature T/T_B, reduced by the transition of the pure B component against volume fraction χ of side chain. At high volume fraction SCs dominate ordering and an N_I phase results. At low χ the converse is true. At χ_o there is a balance between the hinge and SC–MC nematic forces. Within the N_{III} phase there is a critical point (shown as a terminating dot) associated with SC ordering in the field of the main chains. The precise values of the coupling constants is given in Wang & Warner (1987).

volume fraction of side chains make them dominate and we expect N_I and *vice versa.* The most qualitative manifestation of the self order is the form that the chains take; prolate or oblate depending on the ordering influences. Both types have been seen by neutron scattering and spectroscopic techniques, and are of vital concern when dealing with networks. A detailed discussion of the relative influences at work has been given in the other reviews cited.

Such competitive nematic self ordering is conveniently illustrated by a specific phase diagram abstracted from Wang & Warner (1987, figure 3). For the couplings considered, the neutral point where $v_m = 0$ is $\chi_o = 0.166$, with $T_B(\chi_o)/T_B(0) = 0.913$ and $T_A(\chi_o)/T_B(0) = 0.155$. Temperatures are reduced by the transition temperature of the backbone with no SCs attached, $\chi = 0$, that is by $T_B(0)$. At low χ, $T_B > T_A$ and a phase dominated by the backbone obtains, N_{III}. For $\chi > \chi_o$, $v_m < 0$ and N_{II} obtains. Guo *et al.* (1991, 1993) varied composition χ through a family of polymers and explored this region of approximate decoupling.

At high χ where $T_A > T_B$ the SC self ordering dominates to give the N_I phase. Around the volume fraction χ' further cooling can give N_{II} and then a re-entrant N_I, an extra possibility due to the different temperature scaling of the Maier–Saupe and the worm parts of the problem. The variation of coupling to give both N_I and N_{III} phases, that is both oblate and prolate cases, has been achieved experimentally by Mitchell *et al.* (1992). Transitions between N_I and N_{II} are evidently complex: in both phases the BB and SCs are perpendicular, but go between SC and MC dominance. An intermediate possibility is for both parts of the molecule to order, but in perpendicular directions. Distortions introduced by the cross coupling prevent each from being separately uniaxial. Since the ordering directions are perpendicular, the molecular alignment as a whole is highly biaxial. This has been modelled (Bladon *et al.* 1992) since SC polymers offer a good opportunity for biaxiality. In the biaxial case there are four order parameters and the order is very complex. Experimentally such biaxiality has long since been found (Hessel *et al.* 1987).

SC systems often have a backbone with a very weak nematic tendency: the side chains dominate totally and the backbone, say aliphatic, has only induced nematic order from the side chains. It may be more appropriate to model the backbone by a freely jointed chain. In that case the statistical weight (2.3) has the main chain part replaced by the freely jointed part (2.2) to give instead

$$p(\theta) \sim \exp\left[\frac{vQ_A}{k_BT}P_2(\cos\theta) - \frac{U_A}{k_BT}P_2(\cos\theta_A)\right]. \tag{2.5}$$

The backbone appears like a MS system in an external field from the side chains, that is, only Q_A appears in its potential term. We shall not pursue this in this section on side chain melts for *competitive* ordering gives the most interesting forms of self order. We shall discuss the model further under nematic network elasticity.

3. Self order and form in solid liquid crystals

Conventional polymer networks (rubbers and gels) are already a delicate and interesting state of matter before they are given a liquid crystal character as well. Although solids in the sense that they do not flow, they have many of the aspects of liquids, for instance a shear modulus of order 10^5 times smaller than the compressional modulus and the ability to withstand very large strains. The largely entropic basis for rubber elasticity is of course well understood and is an example of where form at the molecular level is reflected in macroscopic shape changes. Entropy drops associated with molecular extension or flattening generate the elastic resistance to imposed strains. Crosslinking nematic polymers solidifies them in the above marginal sense seen in elastomers, and gives rise to materials one might term ‘solid liquid crystals’.

Nematic elastomers have much richer properties than conventional elastomers in at least two regards: (i) because molecular shape change can be spontaneous when ordering takes place, then so can macroscopic strains be spontaneous. Conversely the application of stress to a system in its isotropic phase can induce a phase transition to a nematic state (ii) a self-ordering system already starts with an anisotropic distribution of chain shapes. It can respond to an imposed strain not by changing the shape of the distribution (which is the source of the entropy drop in a conventional, isotropic rubber), but by rotating the distribution. This can be done at zero entropy change and hence no free energy cost. The associated macroscopic strains are not trivial rotations; thus the ‘solid’ is undergoing strain with no stress, in effect our solid liquid crystals can liquify. We shall review these two unique forms of self-ordering separately. There are in addition many quite unusual new transitions (Bladon *et al.* 1993, 1994; Mitchell *et al.* 1993) seen in nematic networks when stress is applied – in some sense the opposite of Fredericks transitions – but these take us beyond our current scope of *self* order and form.

A simplifying (but inessential) approximation is that of affine deformations: chain shape change is in geometric proportion to that of the solid as a whole. For long enough chains the distribution of chain spans between crosslink points is gaussian (albeit anisotropic). A span between links, with its end to end vector, is shown in figure 4. It is shown distorting in geometric proportion to the bulk distortion.

The elastic part of the free energy is then calculated in the usual way, averaging the log of the current (nematic) distribution function over the formation

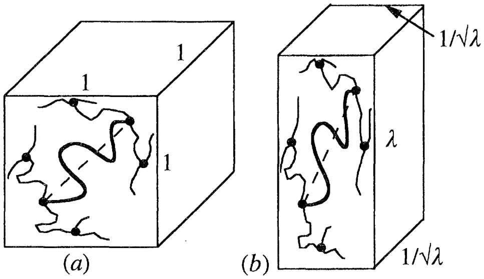


Figure 4. Rubber undergoing a distortion by factors of λ along the z direction and $1/\lambda^{1/2}$ in the two perpendicular directions, thus conserving volume. A test strand (heavier line) is shown attached to neighbouring chains in the network, the end to end vector $\boldsymbol{R}$ spanning these connection points. The average of the log of the probability of such a strand over its formation probability yields the elastic free energy.

conditions and gives

$$F_{el} = \tfrac{1}{2} N_x k_B T \left[\lambda^2 \frac{l^o}{l_\parallel} + \frac{2}{\lambda} \frac{l^o}{l_\perp} + \ln \left(\frac{l_\parallel l_\perp^2}{l^{o3}} \right) \right]. \tag{3.1}$$

Abramchuk *et al.* (1987, 1989), Warner *et al.* (1988). The number of network strands (between junction points) per unit volume is N_x and l^o is the effective step length in the formation state that for simplicity we have taken to be isotropic. The distortion $\lambda_z = \lambda$ is the ratio of the final length in the ordering direction to the initial value. The constancy of volume on deformation demands that $\lambda_x = \lambda_y = 1/\sqrt{\lambda}$ so that the product of the λs (the relative volume change) is unity.

The problem then remains to calculate the effective step lengths $l_\parallel(Q)$ and $l_\perp(Q)$ in terms of the nematic order Q of the backbone. Abramchuk *et al.* (1987, 1989) have used a freely jointed rod model of the polymer, Warner *et al.* (1988) a wormchain. However the principles of nematic rubber elasticity, once these chain shape factors have been calculated, are the same.

The *spontaneous* shape change λ_{m} minimizes the free energy, that is $\partial F_{el}/\partial\lambda = 0$, and is $\lambda_{\mathrm{m}}(Q) = (l_z/l_p)^{1/3}$. It is a function of the nematic order Q which is yet to be determined. For $Q > 0$ (a prolate phase $l_z > l_p$ and hence $\lambda_{\mathrm{m}} > 1$) there is a spontaneous elongation of the sample on cooling from the isotropic to the nematic state. There is a flattening ($\lambda_{\mathrm{m}} < 1$) for the oblate case where $Q < 0$. In figure 4 a block of rubber, with an identified test strand, is shown changing by a factor of λ on going to a prolate nematic state. The final value of Q chosen minimizes the total free energy $F(Q) = F_{nem}(Q) + F_{el}(\lambda_{\mathrm{m}}(Q), Q)$ where $F_{nem}(Q)$ is the nematic free energy of the corresponding melt. In the elastic contribution, F_{el}, the optimal value $\lambda_{\mathrm{m}}(Q)$ has been inserted for λ. This spontaneous change of shape of a stress-free nematic rubber has been observed in monodomain samples by Mitchell *et al.* (1992), and in polydomain samples by Schätzle *et al.* (1989), by observing the stress–strain relation below T_{ni} in stress-aligned samples and extrapolating back to zero stress.

The elastic free energy is an addition to the underlying nematic melt free energy since crosslinking means that chains on becoming nematic cannot adopt their natural nematic melt shape, but one that is a compromise between this and the requirement of constant density. The nematic–isotropic transition temperature for a crosslinked system, $T_{NI}^{(x)}$, is thus lower than the melt value T_{NI}, see Warner *et al* (1988) for theory and Mitchell & Davis (1994) for experiments. For networks formed in the nematic state the transition temperature is raised since a memory of the initial nematic state is frozen in by the crosslinking. Now, when heated to the isotropic state, the chains cannot adopt their natural shape. The energy of the isotropic state rises and the transition temperature $T_{NI}^{(x)}$ is greater than the melt value. Again experiment and theory agree qualitatively.

Of course, to see such interesting effects one must really work with nematic monodomains. They have been made by two routes. A nematic melt can be subjected (Legge *et al.* 1991) to an external field, for instance magnetic, to create a monodomain which is then crosslinked. Alternatively (Küpfer & Finkelmann 1991) a melt can be lightly crosslinked and then stretched by a mechanical field before a second crosslinking. The internal stress thereby created induces a nematic monodomain if the sample is cooled below T_{ni}.

The formation state (over which the current state is averaged) is then no longer given by an isotropic gaussian distribution characterized by one length l^o as in our simple example, and the simple form (3.1) requires generalization. In a nematic monodomain with initial director $\boldsymbol{n}^o$ coincident with the $\boldsymbol{z}$ axis, spans $\boldsymbol{R}^o$ of polymer chain between network points have at the moment of crosslinking the distribution

$$P_o(R^o) \sim \det[l_{ij}^o]^{-1/2} \exp\left(-\frac{3}{2L} R_i^o (l_{ij}^o)^{-1} R_j^o\right), \tag{3.2}$$

where summation over repeated indices has been assumed. The matrix l_{ij}^o of inverse effective step lengths defining the chain shape parallel and perpendicular to the director $\boldsymbol{n}^o$ for a uniaxial phase is

$$(l_{ij}^o)^{-1} = 1/l_\perp^o \delta_{ij} + (1/l_\parallel^o - 1/l_\perp^o) n_i^o n_j^o, \tag{3.3}$$

with eigenvalues $1/l_\perp^o$ and $1/l_\parallel^o$ in its principal frame. The effective step lengths are related to the radii of gyration by $\langle (R_\parallel^o)^2 \rangle = l_\parallel^o (Q^o) L$, etc. (as we have noted for MC systems, often $l_\parallel \gg l_\perp$, but the elastomers examined experimentally have thus far been SC systems where the difference is not extreme). Chain shape clearly depends on the nematic order parameter Q^o at the moment of crosslinking. Let the current span be $R_i = \lambda_{ij} R_j^o$ with λ_{ij} the macroscopic deformation tensor of the whole block of rubber. We consider deformations λ_{ij} imposed with respect to the initial crosslinking state. The incompressibility of rubber in this more general case is expressed by $\det[\lambda_{ij}] = 1$. In general the current temperature may be different from that of the formation state. Span probabilities are governed by a distribution $P(R)$ differing from that in (3.2) only in the $(l_{ij})^{-1}$ tensor, which describes the current chain shape. Taking $F_{el}/k_B T = -\langle \ln P(R) \rangle_{P_0(R^o)}$ that is, the quenched average, one obtains for the elastic free energy per network strand the generalization of (3.1)

$$\frac{2F_{el}}{k_B T} = l_{ij}^o \lambda_{kj} (l_{kl})^{-1} \lambda_{li} - \ln\left(\frac{\det[\underline{\underline{l}}^0]}{\det[\underline{\underline{l}}]}\right) \equiv \mathrm{tr}[\underline{\underline{l}}^o \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{l}}^{-1} \cdot \underline{\underline{\lambda}}] - \ln\left(\frac{\det[\underline{\underline{l}}^0]}{\det[\underline{\underline{l}}]}\right). \tag{3.4}$$

The current director, denoted by $\boldsymbol{n}$, is coincident with the initial $\boldsymbol{n}^o$ if λ_{ij} has its principal frame aligned with $\boldsymbol{n}^o$. In that case λ_{ij} has the simple diagonal structure we assumed before. Minimization of (3.4) gives the spontaneous relaxation of deformations. The previous result for the shape change is simply generalized to an anisotropic starting point:

$$\lambda_{\mathrm{m}} = \left(l_{\|} l^{o}_{\perp} / l^{o}_{\|} l_{\perp}\right)^{1/3} \tag{3.5}$$

(see Warner *et al.* 1988). Mitchell *et al.* (1993) have examined these kinds of spontaneous shape changes by heating nematic rubbers into the isotropic phase. Even after prolonged periods at high temperatures, the network on cooling will undergo a spontaneous shape change to its original form. The nematic order is permanently recorded by the crosslinking.

If now a strain (extensional or shear) is imposed with its principal directions not coincident with those of the original state, the director is forced to rotate (Bladon *et al.* 1993). In some cases this rotation is continuous as strain is increased. For some relative orientations of $\boldsymbol{n}_o$ and the strain axes the response is discontinuous, the rotational barrier created by the crosslinking being overcome at a critical strain (Bladon *et al.* 1993, 1994). This elasticity where strain and internal rotation are coupled was anticipated by de Gennes (1980) for nematic elastomers behaving as 'solid liquid crystals'. What he did not envisage in his continuum description was the above instabilities that occur at the high distortions of which elastomers are capable. For this highly nonlinear régime a molecular theoryis of the essence. We return, however, to aspects of self ordering, rather than reactions of elastomers to imposed fields.

If we wish to examine deformations, $\underline{\underline{\lambda}}$, that do not agree in their principal axes with the original orientation, $\boldsymbol{n}^0$, then the anisotropic step length tensor after the deformation, l_{ij}, may differ from l^0_{ij} in both magnitude and orientation of its principal values, reflecting a new equilibrium state with $\boldsymbol{n}$ at some angle θ with respect to $\boldsymbol{n}^0$. θ is a function of the magnitude of deformation and of the orientation, α, of the frame of the deformation λ_{ij} with respect to $\boldsymbol{n}^0$. To identify the equilibrium state one minimizes F_{el} with respect to any free components of $\underline{\underline{\lambda}}$ and with respect to Q and θ, which characterize the underlying nematic order $\underline{\underline{Q}}$.

The least constrained deformation is a strain λ imposed in one direction $\boldsymbol{u}$, at angle α to the original director, with all other strains free to relax, see figure 5.

One finds $\boldsymbol{n}$ rotates with increasing λ but that the free energy does not rise until $\boldsymbol{n}$ lies along the principal direction u of $\underline{\underline{\lambda}}$, at which stage the distortion has reached the value λ^*, Warner *et al.* (1994). This is essentially the behaviour of a liquid, albeit a liquid with a rotating structure. Thereafter the free energy rises as for a classical isotropic elastomer starting its deformation at this point. Details of the calculation are given by Warner *et al.* (1994). The critical strain $\lambda^*(\alpha)$ depends on the misalignment, α, of the strain and the initial director:

$$\lambda^*(\alpha)^2 = \tfrac{1}{2}\left[\lambda_c^3 + 1 - (\lambda_c^3 - 1)\cos 2\alpha\right]. \tag{3.6}$$

Thus the free energy for $\lambda < \lambda^*$ is

$$2F_{el}/k_B T = 3 \tag{3.7}$$

and then rises for $\lambda > \lambda^*$ as

$$\frac{2F_{el}}{k_B T} = \frac{\lambda^2}{\lambda^{*\,2}} + 2\frac{\lambda^*}{\lambda}. \tag{3.8}$$

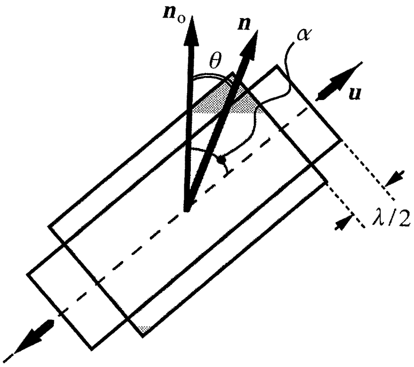


Figure 5. Alignment geometry in the (x, z) plane for an extension by a factor λ along the unit vector u. n_0 and n are initial and current directors respectively.

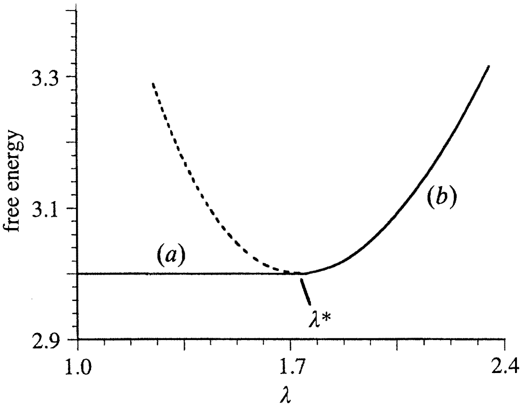


Figure 6. The elastic free energy per network strand (in units of $\frac{1}{2}k_BT$) against distortion λ imposed at an angle $\alpha = \pi/2$ to the original director. The free energy is flat (branch (a)) for $1 < \lambda < \lambda^*$ with the critical λ^* depending on the misorientation α. For $\lambda > \lambda^*$the free energy increases as for a classical rubber about the point $\lambda = 1$ (branch (*b*)).

This branch of the free energy has a minimum of 3 at $\lambda = \lambda^*$ and behaves thereafter as a classical elastomer (with an apparent natural shape of $\lambda = \lambda^*(\alpha)$) for $\lambda > \lambda^*$, see figure 6.

The ability for this type of solid to distort at constant free energy is a remarkable consequence of nematic self ordering of polymer chains. As polymers distort at the molecular level to a prolate spheroidal shape they can respond to macroscopic shape change by rotation of their distributions rather than by an entropically expensive bias as isotropic polymers do. Thus the expectation of de Gennes (1980), that crosslinking chains into a network while they are anisotropic in shape will create a memory of this anisotropy and its direction, can sometimes lead to a resistance to director rotation but undersome circumstances the rotational barrier does not exist. It can be simply shown (Warner *et al.* 1994) that this soft response is indeed a rotation at constant entropy.

Such an exact cancellation of any resistance to an external stress (for deformations $\lambda < \lambda^*$) is a feature of a theory specifically based on gaussian chains and the affine deformation approximation. In practice one would perhaps observe a small resistance caused by other effects: in more sophisticated models of rubber elasticity, involving entanglements and correlations, there is probably some resistance. Experimental evidence from nematic elastomers subjected to electric fields suggests that the effects of entanglements and correlations are indeed small, an assertion of importance to conventional elastomers, where entanglements and correlations have been long discussed. Modest electric fields apparently cause large deformations of the solid. Our prediction offers a method of examining these effects in isolation since the crossover at $\lambda = \lambda^*$, figure 6, should be clearly detectable by experiment. Recently a general analysis of the 'soft distortions' has been carried out by Olmsted (1994). He shows that these distortions are examples of deep symmetries characteristic of a uniaxially anisotropic system where the internal degree of freedom creating the uniaxial order can respond to external fields. This question has been examined in some generality by Golubovic & Lubensky (1989).

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Discussion

A. KELLER (*University of Bristol, U.K.*). Spontaneous extension does not necessarily require the existance of a nematic phase. Crystallization from an orientated amorphous state, such as created by stretching rubber, leads to longitudinal self extension if crystallization takes place at constant stress (and to stress relaxation if it occurs at constant length). Also, in some early works Mandelkern introduced cross-links into a highly drawn fibre of polyethylene. On melting the fibre shrunk (as usual) but spontaneously re-extended on crystallization when the molten thread was cooled, when crystallization set in. Thus the crystals re-established the system as it had been originally when the cross-links were introduced. This whole process was reversible, in fact could be used to convert thermal energy into mechanical work.

M. WARNER. I agree that spontaneous distortion in general requires only a permanent memory of an anisotropic state of the system. The naturally nematic melt that I describe, and the system crosslinked with partially crystalline that you describe, are two extreme examples. A more marginal one would be an elastomer crosslinked in two steps, a strain being imposed before the second step. We believe that even such a simple and weakly anisotropic system would have unusual responses to electric fields in the way I have suggested for nematic elastomers. We are in the process of calculating the details of the response.

E. D. T. ATKINS (*University of Bristol, U.K.*). Are you aware of the phenomenon of spontaneous extension when a uniaxial prestrained film or yarn of cellulose acetate is placed in a swelling agent. Spontaneous extensions of up to

500% have been reported. X-ray diffraction shows that the original unoriented prestrained sample becomes oriented after spontaneous distortion (see, for example, Atkins *et al.*, *Proc. 5th Int. Conf. on Dissolving Pulps.* Vienna: TAPPI (1980)).

M. WARNER. I had heard of this work but have not myself seen it. These are indeed fascinating results that would be a challenge to explain theoretically.

E. L. THOMAS. A possible application for such liquid crystalline elastomers might be as some sort of actuator. But since the force is small the work done is small. Perhaps optical switching where the relatively large displacement could be used to advantage is more promising?

Y. K. GODOVSKY (*Karpov Institute of Physical Chemistry, Moscow*). The nematic liquid crystalline elastomers are composed either of stiff rods (mesogenic groups) linked into the main chain by flexible spacers, or attached as side chains. A number of unusual phenomena have been predicted theoretically, including phase transitions, spontaneous shape changes, discontinuous stress strain relations, nonlinear stress-optical behaviour. Some of these predictions have been found experimentally in the studies of H. Finkelmann (University of Freiburg, Germany). By crosslinking the mesophase polysiloxane it is also possible to obtain mesophase elastomers, which also show some unusual phenomena under deformation. I will mention and demonstrate only one aspect of stress-strain behaviour of these mesophase elastomers: stress-induced mesophase formation in slightly crosslinked PDES. During stretching of initially amorphous films the strain-induced mesophase occurs, which can be identified by various methods such as defomation calorimetry, stress-optical measurements, etc. The most remarkable feature of this behaviour is the fact that during the cyclic deformation necking–denecking phenomena occur. Because of a very small energy change, resulting from the stress-induced mesophase formation during contraction, immediate isotropization occurs.

A. H. WINDLE. Normally, the plot of true stress against draw ratio for a rubber continues to climb steeply so tht it is impossible to construct a tangent to it from the origin of the plot (at draw ratio 1). Considerés construction is thus not possible, and the rubber will deform uniformly, with no necking, right up to fracture. The implication of the observed propagation of the Luder's band is that the strain induced transformation to a crystalline mesophase, as indicated by X-ray diffraction, flattens the stress-strain relation sufficiently to enable the tangent construction to be fmade. The bands appeared to move along the sample rather rapidly in relation to the applied extension rate and thus will be associated with a comparatively small strain increment. This fact would suggest that after the transformation induced strain increment, the stress/strain curve becomes rapidly steeper as the harder mesophase is formed. It would be interesting to see such curves, especially plotted as true stress.