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Liquid Crystalline Polymers: Self-Organization and Assembly

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Liquid crystalline polymers: self-organization and assembly

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Liquid crystal forming monomers, typically rods, can be polymerized to form long mesogenic molecules. In contrast to simple rods, these polymers often have internal degrees of freedom so that they display the subtle behaviour of both high polymers and simple liquid crystals. They can have the rod elements either concatenated as a back-bone to give main chain (MC), or pendant to a back-bone to give side chain (SC) liquid crystals, or both. The physics unique to liquid crystalline polymers (LCPS) comes from their shape being dependent on the state of nematic order. Simple systems remain molecular rods (or disks) on ordering whereas a chain extends or flattens (depending on whether or not the nematic order is prolate or oblate). New phenomena as a result of this occur in situations as disparate as networks and, it is predicted, in dielectric response. We examine both SC and MC LCPS and the mechanisms by which they order lyotropically (in solution) and thermotropically (in the melt). Various types of models will be discussed in general and then restricted to the thermotropic case, lyotropic systems being discussed in Lekkerkerker & Vroege (this volume). The transition to the ordered state is first order as in simple nematics. The main characteristics of this state are modified chain conformations and, additionally for side chain polymers, transitions between various novel competing nematic states. A form of self-assembly that is a delicate function of the nematic order is observed in transesterifying LCPS. The number of chain ends is conserved but material exchanged between chains according to whether they are in the isotropic or nematic state. We review a model of this type of self-assembly.

1. Introduction

Liquid crystalline polymers (LCPS) are materials with unusual properties stemming from the combination in one molecule of two antipathetical characters, liquid crystallinity and high polymer conformational entropy. The simple rods of conventional nematics are largely inflexible. Their molecular shape remains unchanged on orientational ordering. LCPS in contrast spontaneously change their shape on ordering. This is unknown in conventional polymers where, however, shape change is the principal agent of physical response, for instance in driving the elastic resistance to deformation of an elastomer or the visco-elastic response of a polymer melt in flow. It is thus not surprising that spontaneous shape change invokes novel behaviour not found in liquid crystals or in polymers separately. These new possibilities were anticipated by de Gennes (1975) in the most extreme context for polymer shape change, that is networks. de Gennes (1982) later labelled the nematic and the polymer entropy characters as 'antagonists'. The essential element is the combination of internal flexibility and nematogenic tendencies. Thus we shall not discuss LCPS that are simply very long, but essentially inflexible, rods. These are

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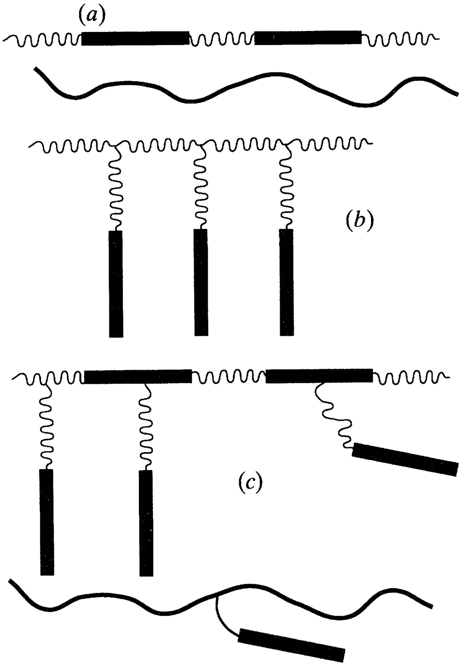

Figure 1. Possible types of LCPs. Rodlike (mesogenic) elements connected by more flexible spacers and hinges. (*a*) Main chain LCPs with the mesogenic elements in the chain backbone separated by spacers. (*b*) Side chain LCPs with the mesogenic elements pendant as side chains. (*c*) Combined LCPs with stiff elements in both the backbone and as side chains. The connection via a hinge is shown to be at a flexible or at a stiff part of the backbone. One of the hinges is shown bent. Below (*a*) and (*c*) are shown worm, and worm plus hinge and rod models of these molecules, where the MC stiffness is distributed.

extreme forms of conventional nematics and are very well described by Onsager (1949) theory in the dilute limit or by Flory (1956) lattice theory in the more concentrated case.

(*a*) *Systems*

Nematic forming rods can be incorporated into a polymer as elements of the backbone, so-called main chain (MC) LCPs, or as pendant elements to a flexible backbone, side chain (SC) LCPs, or with both types of elements (combined LCPs). They can be schematically represented as in figure 1*a*–*c*.

A good example of main chain LCPs with sufficient internal flexibility to be an isotropic gaussian above and an anisotropic gaussian below its phase transition is DDA, first synthesized by Blumstein, see d'Allest *et al.* (1988), who also show the neutron scattering evidence for the shape change in the melt. The chain elongates in the direction of ordering and is thus prolate spheroidal in shape. Some SC systems where the hinge is naturally bent, or because in combined systems the backbone and side chains are nematically inspired to be parallel, are also prolate. For many purposes they can be thought of as MC systems. See figure 2*a* for a schematic picture of prolate nematic phases.

Side chain LCPs were first realized by Shibaev and later by Finkelmann *et al.* The vast range of chemical types synthesized have been reviewed at length in a series of articles in the book by McArdle (1989) devoted to SC LCPs. Some order in a prolate way as discussed above. When the SC rods dominate the ordering and the backbones

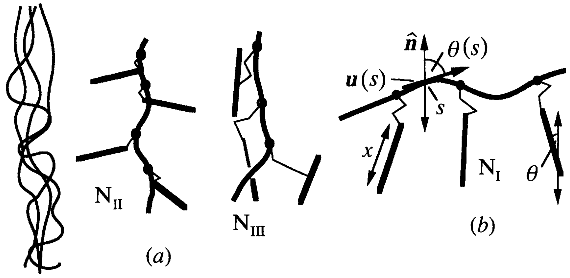

Figure 2. Prolate and oblate phases of LCPs. (*a*) Three prolate phases, a MS phase and two SC phases $\mathrm{N_{II}}$ and $\mathrm{N_{III}}$, where the chain is elongated along the ordering direction. Note in the latter that the hinges are either bent (naturally or by the nematic field) or the attachment is perpendicular. (*b*) The $\mathrm{N_I}$ phase where the SC ordering is dominant and the perpendicular hinge forces the backbone to be oblate, that is flattened. The director $\boldsymbol{n}$, common to all the figures is shown in (*b*), as are the definitions of the local chain direction $\boldsymbol{u}$ at the arc point s and the direction of a SC element. The relevant angles θ with the director are indicated. These definitions are appropriate to the other cases also.

are constrained to be on average perpendicular to the rods, the chains (see figure 2*b*) are of necessity flattened to an oblate shape, as first seen in neutron scattering by Kirste & Ohm (1985) and Keller *et al.* (1985). Wang & Warner (1987) have termed this phase $\mathrm{N_I}$, see McArdle (1989, ch. 2) for an extensive review of these various new nematic phases. Discussed there is the evidence for both parallel and perpendicular coupling from Koch *et al.* (1985) and Schätzle & Finkelmann (1987). A lattice picture of these types of phases was discussed by Vasilenko *et al.* (1985).

The important point is that, if we concentrate on the polymer backbone, it can be of prolate or oblate symmetry in the nematic phase, that is with positive or negative nematic order parameter Q. The latter is not possible for simple nematics and is possible here only because we really have another prolate nematic (the side chains) driving the polymeric part of the problem.

(*b*) *Motivation for studying* LCPS

Much of the motivation for studying LCPs arises from the exploitation of SC forms as media for nonlinear optics. Side chain rods, being frequently conjugated to provide stiffness, can be made into excellent chromophores. Nematic order increases the efficiency of the poling for $\chi^{(2)}$ and is itself the order required for $\chi^{(3)}$ response. Since the rods are connected to the polymers they cannot phase separate from them, the usual problem when using polymeric hosts for large concentrations of dye. There are problems though of subsequent temporal stability. Although in a polymer glass gross motions of chains cease at the glass transition, the poled order of the rods can be released by local motions which may still be active. MC LCPs would not suffer this disadvantage and it has been speculated that they may have considerable other advantages (Warner 1989*a*, *b*).

Other opto-electronic applications where polymeric attributes are attractive are also a motivation, for instance for free standing films, very slow response, laser read–write capability, free standing films (including ferro-electrics) and so on. Elastomers, made from LCPs are currently under much study, motivated partly by their intrinsic interest (we shall later describe their unusual properties) and partly because of new applications in the area of mechanico-optical and mechanico-thermal coupling.

2. LCP ordering: mechanisms and their modelling

(*a*) *Simple systems*

Conventional nematics order for two reasons, often of comparable importance.

(i) Packing requirements (lyotropics in solution with transitions controlled by concentration): At high concentrations rods can easily overlap. They can maximize their translational entropy at the expense of reducing rotational entropy, that is by partly aligning. This was recognized first by Onsager (1949) who treated rods sufficiently long that they then began to overlap and form a nematic state while dilute enough to still be interacting only in pairs, in other words a second virial approach. An alternative (Flory 1956) is to model rods by putting them on a lattice and evaluate their positional freedom when they overlap with others. Thus the Flory theory can be applied to short rods which must be in dense solution before nematic effects become important. In the melt this approach yields a critical axial ratio, x_c. Steric effects for rods longer than this are so strong it is impossible to achieve the isotropic state at any temperature. Values of x_c differ according to precisely which approach is adopted and range between 8 and 3.5.

(ii) Orientational dependent potentials (thermotropics in the melt with transitions controlled by temperature): Liquid crystal molecules always have a shape anisotropy with an associated electronic anisotropy, for instance conjugated bonds extending along the rod axis. Such fluctuating electron systems create van der Waals attractions between molecules, strongest when two rods are parallel or antiparallel and weakest when they are at 90°. The Maier–Saupe (Maier & Saupe 1958) theory of liquid crystals rests entirely upon this interaction. It is the only mechanism for a transition in a melt where the concentration is essentially fixed (relative density changes by typically less than 0.004 at the transition).

(iii) In practice both influences are important (Warner 1980) and models take both soft and hard forces into account. Thus rods with $x < x_c$ can still order. As T is reduced the soft forces increasingly provide the additional impetus for ordering.

The single rod distribution function for a rod at an angle θ to the ordering direction (z) in both (i) and (ii) is of the form $p(\theta) \sim \exp[-Cf(\theta)/k_B T]$ where $f(\theta)$ has the up–down symmetry of liquid crystals, $f(\theta) = f(\pi-\theta)$, and is $f(\theta) \sim -P_2(\cos\theta) \equiv -(\frac{3}{2}\cos^2\theta - \frac{1}{2})$ in MS theory, $f(\theta) \sim \sin\theta$ in Flory theory and so on. Onsager took $p(\theta) \sim \cosh(C\cos\theta)$ which achieves the same result of having rods biased toward $\theta = 0$ or π in the ordered state. The constant C either reflects the geometry (axial ratio) of the rods in packing theories, or the strength of the van der Waals interaction. It is proportional to the mean order in mean field models, $Q = \langle P_2(\cos\theta)\rangle$ or an equivalent order parameter ($y \sim \langle \sin\theta \rangle$) in Flory theory and similarly in other theories. Additionally, in packing theories C is proportional to $T, C = C_0 k_B T$ so that $p(\theta) \sim \exp[-C_0 f(\theta)]$ is an athermal expression, simply reflecting the entropy of packing. For a qualitative analysis of the new phenomena arising in LCPs it is preferable not to get involved with the minutiae of nematic theory, but simply to take $p(\theta) \sim \exp[CQP_2(\cos\theta)/k_B T)]$, where it is understood that C absorbs both packing and van der Waals effects and that $P_2(\cos\theta)$ reflects the symmetry of the true p. The mean order Q has been extracted since this is a mean field potential.

Such a Maier–Saupe like theory that simulates this simplified model of all interactions has the nematic–isotropic phase transition temperature set by $k_B T_{NI} = 0.22C$ and $Q_{NI} = 0.43$. It sets a temperature scale quite different from that of worms and the comparison of the two scales is central to competitive nematic ordering in SC

Figure 3

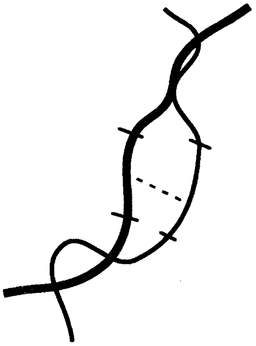

Figure 4

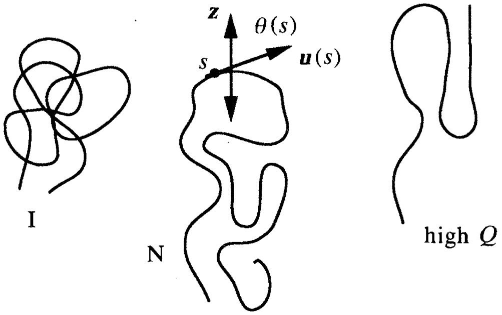

Figure 3. In estimating the steric exclusions between two test segments problems arise in the interaction of spatially correlated neighbouring segments on the chains involved.

Figure 4. Various conformations of a main chain LCPs. I denotes the isotropic phase with a spherical conformation. N is the nematic state with orientational order stretching the chain along the ordering direction z. The chain tangent vector $\boldsymbol{u}(s)$ at the arc point s is shown to make an angle $\theta(s)$ with z. In the high Q (high order) limit, the chain is stretched out with rare hairpin reversals in direction.

LCPs. Experimentally the order parameter at the transition Q_{NI} is not universally 0.43, indicating that steric effects are indeed important and that this model is only of qualitative significance.

(*b*) *Application of these models to LCPs*

(i) *Main chain LCPs*

It is not straightforward to apply to LCPs the above methods of calculating the steric effect of one chain on the packing of another. What section of the chain does one consider as a quasi-independent rod to take over the results of Flory and Onsager? The obvious measure is the effective step length. It is clear, however, that there are spatial correlations between such a persistent segment of a chain and the parts of the chain that precede and follow it along the arc sequence of the chain. These chemical neighbours will also overlap with the equivalent neighbours of a segment on another chain so that the steric interaction of two such test segments will be influenced by the interactions of their associated segments; see figure 3. These questions have been addressed by a large number of workers, notably Khokhlov, Semenov, Shibaev, Odijk, Lekkerkerker and co-workers. For lyotropic systems where concentration dependence of packing effects is critical, these questions are reviewed in Lekkerkerker & Vroege (this volume) and in the article by Khokhlov & Semenov (1988). However, following the previous section, we shall represent the nematic field simply by the P_2 function and an effective hard and soft coupling constant. We shall henceforth only consider melts, that is where there can be no further concentration variation.

We shall describe the chain by a worm of length L and with a bend constant ϵ. A worm has a tangent vector $\boldsymbol{u}(s)$, a unit vector specifying the local direction of the chain. The probability distribution of chains is then

$$p(\theta) \sim \exp\left[-\frac{\epsilon}{k_{\mathrm{B}}T}\int_0^L \mathrm{d}s\,\dot{\boldsymbol{u}}(s)^2 + \frac{aQ}{k_{\mathrm{B}}T}\int \mathrm{d}s\,P_2(\cos\theta(s))\right], \qquad (1)$$

where the dot indicates $\partial/\partial s$, $\theta(s)$ is the angle the chain makes with the ordering direction (see figure 4) and a is the nematic coupling per unit arc length of chain. Such persistent chains are gaussians if $L > l_0$, the persistence length in the isotropic state, $l_0 = \epsilon/k_B T$. In the isotropic state they have $\langle R^2 \rangle = l_0 L$ and in the nematic state have $\langle R_z^2 \rangle = l_z L$ and $\langle \boldsymbol{R}_p^2 \rangle = 2 l_p L$ in the perpendicular direction. The elongation is thus seen in the growth of l_z. 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, see figure 3. Changes of direction along the nematic field are penalized by bend energy if they are too rapid, and by nematic fields if they are too slow. The optimum change of direction at zero temperature is the hairpin, with energy $U_h = (\epsilon a)^{\frac{1}{2}}$. Crudely one can say that hairpins occur with a frequency along the chain of $l_0^{-1} \exp(-U_h/k_B T)$. The rapid growth of chain dimensions seen by d'Allest *et al.* (1988) below the nematic–isotropic transition is possibly a signal of hairpins.

The phase transition in nematic worms is at $k_B T_{NI} = 0.388\sqrt{(a\epsilon)}$ with $Q_{NI} = 0.35$ at the transition. The remarks made above about non-universality hold here too. The characteristic temperature scale $\sim \sqrt{(a\epsilon)}$ is quite different from that of the SC part of the problem.

(ii) *Side chain polymers*

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

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

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

$$U_A = -x[\chi v_A Q_A + (1-\chi)\, v_m Q_B], \quad U_B = -[(1-\chi)\, v_m Q_A + \chi v_B Q_B]. \tag{3}$$

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 $x v_A$, where v_A is a nematic coupling per unit length ($x v_A \equiv C$ of the discussion of nematic ordering). Complex ordering is possible with two order parameters, see the original papers Vasilenko *et al.* (1985) and Wang & Warner (1987). The review by Warner in McArdle (1989) gives a qualitative discussion. In the biaxial case there are four order parameters and the order is still more complex (see Bladon *et al.* 1992).

The potentials show each component to be in a nematic field due to the ordering of its own type and the nematic field due to the other species, the latter effectively like an external field. Concentrating on the self fields, the relative values of the characteristic temperature $k_B T_B = 0.388(1-\chi)\sqrt{(v_B \epsilon)}$ of the BB and that of the SC,

$k_B T_A = 0.22\chi x v_A$, will determine which species will order first and force the other to follow in a paranematic fashion as if it were in an external field. The other can possibly suffer a phase transition at a lower temperature approximately equal to its own characteristic temperature. Details depend on the cross coupling, as we shall discuss by example in the next section.

The mutual coupling contains two influences, the backbone–side chain nematic coupling driving the two to be parallel (a positive contribution to v_m) and the effect of the hinge. If the hinge tends to orient the side chain at right angles to the backbone, then this contribution to v_m is negative. The contribution is positive if the hinge is naturally bent and drives the two to be parallel. Overall we have $v_m = v_c - v_f/[x(1-\chi)]$, where v_c is the nematic cross coupling and v_f is the effect of the hinge; see Wang & Warner (1987) for a full discussion of how v_m is composed. In fact the theory really only depends on the three couplings v_A, v_B, v_m. We display the components of v_m to illustrate the factors that control competitive ordering and how they can be varied. The volume fraction $\chi_0 = 1 - v_f/xv_c$ is special since there $v_m = 0$ and the two parts act as if effectively decoupled (at least within this model with its simplification of steric and hinge effects).

Positive v_c is straightforward since all three influences drive the backbone 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 species that is dominant adopts a positive order parameter, the other is forced by the hinge to have a negative order parameter. One can see this geometrically in figure 2*b* where the phase N_I has dominant side chains and the backbone is pressed down to a flattened (oblate) form. In N_{II} (figure 2*a*) the converse is true and side chains resemble the bristles on a bottle brush with the backbone in a prolate (dominant) phase. As the volume fraction χ of side chain changes, then so does this balance. High volume fraction of side chains make them dominate and we expect N_I and vice versa. Changing χ also changes the character of v_m since the strength of the nematic interaction relative to the hinge strength can be altered. It is possible to analyse the phase possibilities with a Maxwell area construction that is exhaustive and also gives analytic criteria for critical points and the slopes of phase boundaries (Renz & Warner 1988).

(iii) *Other models*

The polymeric part of this problem has been modelled by distributing the stiffness continuously along the chain, in contrast to, say, lattice models where one has joints (with some stiffness) connecting rigid segments. Within the scheme of distributed stiffness it is possible to have one further simplification: length non-conserving models. Any continuous curve with position vector $\boldsymbol{r}(s)$ has a unit tangent vector $\partial \boldsymbol{r}(s)/\partial s \equiv \boldsymbol{u}(s)$, that is $\boldsymbol{u}(s)^2 = 1$ (sketching a change in position Δr and the corresponding change in arc length Δs required will show that in the limit the quotient $\Delta r/\Delta s$ is unity). In contrast a Wiener–Edwards chain, which is gaussian at all length scales including the arbitrarily small, does not have this property. In fact arbitrarily rapid changes in direction are possible. For conventional polymers where one is interested in longer length scale phenomena this is not a problem and such W–E models are excellent. Here, although the local direction of the chain is not defined, and it is via its direction that a nematic chain couples to its neighbours, one can put in the constraint that on average $\boldsymbol{u}(s)$ is a unit vector and recover nematic-like properties: an order parameter, first order transitions and chain anisotropy (see

Ronca & Yoon 1982; Yurasova & Semenov 1991; Gupta & Edwards 1993). For high order one finds that chains stretch out quite differently from how worms (via hairpins, discussed above) or discrete models of chains stretch (transfer matrix techniques have been used to analyse discrete models in their limits (see Warner & Wang 1992)). The essential difference is that a chain that only conserves length globally can decide locally not to put arc length where it is unfavourable, for instance in the hairpin-like regions of chain reversal. The exponential character of the growth is lost.

3. Illustrations

(a) *Chain conformations*

We have discussed already that chains become anisotropic in their nematic state, either prolate or oblate, and have cited the experiments that measure this. The observation of an extreme form of prolate anisotropy, presumably associated with infrequent hairpin changes of direction, has been cited. Higgins *et al.* (1992) and Cotton *et al.* (1993) also observed MC anisotropy. Extreme oblate anisotropy has been predicted (Renz & Warner 1986; Kunchenko & Svetogorski 1986) to exist in well-ordered SC smectic polymers where chains could become confined toward layers of the smectic ordering of the SCs to which the backbone is attached. This has been seen by Moussa *et al.* (1987) and further theory carried out by Rieger (1988, 1989).

(b) *Molecular dynamics*

The dynamics of how LCPs change their conformations has not received much attention. It is an important area since the knowledge of dynamics should underpin any molecularly based model of LCP rheology, and such dynamics control important processes such as poling for nonlinear optics.

MC LCP dynamics are presumably extremely complex, unless chains are very weakly ordered and execute an only slightly modified Rouse or reptation dynamics. As order gets stronger the connectedness of the chain means that it can essentially move only along its own length. Thus the motion at one point on a chain requires the motion of a large part of the chain as a whole, that is the dynamics are highly non-local. A 'rope and pulley' model (Williams & Warner 1990) of the dynamics in the hairpin limit has this extreme non-locality. The motion of all the chain between two successive hairpins is required to move a given arc point on a chain, and this is thus slow. Consider a chain with just one hairpin and this is near one end (thus the chain resembles a walking stick). To transfer the hairpin to the other, as required in say poling, requires the motion of the arms of the hairpin. The shorter arm moves the most rapidly since the drag, ν, associated with the arm motion is proportional to the length of chain moved parallel to itself. The average length of an arm is of order $\frac{1}{3}L$ whence $\nu \sim \frac{1}{3}\nu_0 L$ when the diffusion constant for curvilinear hairpin motion is $D_{\mathrm{hp}} \sim k_{\mathrm{B}} T/\nu_0 L$. The time taken to diffuse a length of order L from one end of the chain to the other is the renewal time for conformations $\tau_{\mathrm{ren}} \sim L^2/D_{\mathrm{hp}} \sim L^3$. Entanglement of hairpins would make this even slower. NMR experiments on the frequency dependence of line broadening (Zeuner *et al.* 1992) show an anomalous power $\sim \omega^{0.65}$. This does not seem to correspond to the various signatures of hairpin mediated broadening (Warner & Williams 1991) nor to the exponents anticipated from collective effects such as director fluctuations. From their data modelling Zeuner *et al.* (1992) opt for hindered local rotations. Müller *et al.* (1990) give an extensive review of NMR applied to LCPs (of both types).

SC dynamics in the extreme oblate limit, for instance in the smectic phase corresponding to N_I, has been speculated to consist separately of motion of the chain BB and of the SC elements. A model for the latter has been developed (Liu & Warner 1989) where the backbone must be twisted by 180° if individual side chains are to have their orientation along the nematic field reversed. These reversals cost energy, since both torsion and the nematic field are involved, one can think of them as the torsional equivalent of hairpins. The motion of one down a chain would turn the whole chain over. Since the drag on a defect is local, that is ν does not depend on L, then $\tau_{\mathrm{ren}} \sim L^2$ and the renewal of conformations is more rapid than it is for MC LCPS.

(*c*) *SC LCP phase diagrams*

Qualitative features of the competitive nematic ordering leading to new nematic SC phases are best discussed via specific phase diagrams. A sketch of one take from Wang & Warner (1987) is shown in figure 5. For the couplings given, the neutral point is $\chi_0 = 0.166$, with $T_B(\chi_0)/T_B(0) = 0.913$ and $T_A(\chi_0)/T_B(0) = 0.155$. All temperatures are reduced by the transition temperature of the backbone with no SCs attached, $\chi = 0$, that is by $T_B(0)$. Clearly in this region of composition a phase dominated by the backbone will be obtained on cooling from the isotropic phase, that is N_{III} where $v_m > 0$ for $\chi < \chi_0$ and conversely N_{II} for $v_m < 0$. Guo *et al.* (1991, 1993), by varying composition χ through a family of polymers, has explored this region of approximate decoupling. For $v_m > 0$ (that is SCs directed to be parallel to the ordered BBs) as we lower T we eventually reach $T \sim T_A$ and Q_A jumps to values higher than those simply induced by the cross-coupling to the BB ordering. This is the phase line extending to within the N_{III} region. First order systems in an external field display a line of transitions ending with a critical point (shown on the figure). One cannot, of course, look for a critical point on such a composition diagram, but the figure indicates that one has regions where there would be additional low temperature transitions within the N_{III} phase. For $\chi > \chi_0$ the N_{II} phase is bounded below by N_{III}. The natural self-ordering of the SCs which eventually sets in as T is lowered to around T_A overcomes the negative v_m (perpendicular hinge) and the SCs go from negative to positive nematic order.

At still higher χ where $T_A > T_B$ the SC ordering dominates and, on cooling down from I, an N_I phase is encountered. Around the volume fraction marked χ' further cooling can give N_{II} and then a reentrant N_{III}. This extra possibility is 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 has been achieved experimentally by Mitchell *et al.* (1992).

How does a system make transitions between, say, N_I and N_{II}? In each case the BB and SCs are perpendicular. In going between the phases one goes between SC and MC dominance. We have only spoken thus far of uniaxial possibilities, but an intermediate possibility would be for both parts of the molecule to order, but in perpendicular directions. To within the distortions introduced by the cross coupling, each is separately uniaxial but 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. Experimentally such biaxiality has been found (Hessel *et al.* 1987). Space does not allow us to review these complex states.

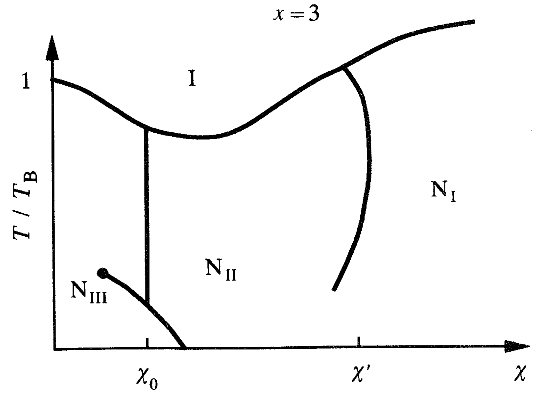

Figure 5. Reduced temperature T/T_B versus volume fraction χ of side chain. The coupling constants are in the ratio $v_A : v_B : v_c : v_f : \epsilon = 1:2:1.2:3:2$. The side chain rod length is $x = 3$. At high volume fraction SCs dominate ordering and an N_I phase results. At low χ the converse is true. At χ_0 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. Phase re-entrancy is located by the volume fraction χ'.

(*d*) *Rubber elasticity*

Most properties unique to polymers stem from the changes in free energy when chain shape is modified. Since one is often only biasing otherwise random conformations, mostly these free energy changes are largely entropic. Rubber elasticity is a leading example. Chains in the network are distorted by the application of mechanical stress and the drop in entropy is simply dependent upon geometrical factors. This aspect makes the physics of nematic networks utterly unlike that found in conventional liquid crystals.

Although rubber is a solid in the sense it will not flow, it is liquid-like because of the high mobility of its molecules, and huge deformations are possible. Deformation takes place at constant volume since the modulus of rubber is only *ca.* 10^6 N m^{-2} compared with *ca.* 10^{10} for conventional solids where volume change is involved. One can think of nematic elastomers as 'solid liquid crystals'.

The affine deformation approximation that chains change shape in geometric proportion to the solid as a whole, the gaussian (albeit anisotropic) distribution for chain shape, and the constancy of volume on deformation make the elastic part of the free energy trivial to calculate:

$$F_{el} = \tfrac{1}{2} N_x k_B T \left[\lambda^2 \frac{l_0}{l_z} + \frac{2}{\lambda} \frac{l_0}{l_p} + \ln \left(\frac{l_z l_p^2}{l_0^3} \right) \right] \tag{4}$$

(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_0 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. Incompressibility demands that $\lambda_x = \lambda_y = 1/\surd\lambda$ so that the product of the λs (the relative volume change) is unity.

The problem then remains to calculate the effective step lengths $l_z(Q)$ and $l_p(Q)$ in terms of the nematic order Q. Abramchuk *et al.* have used a freely jointed rod model of the polymer, Warner *et al.* a worm chain. The principles of elasticity, once these chain shape factors have been calculated, are the same.

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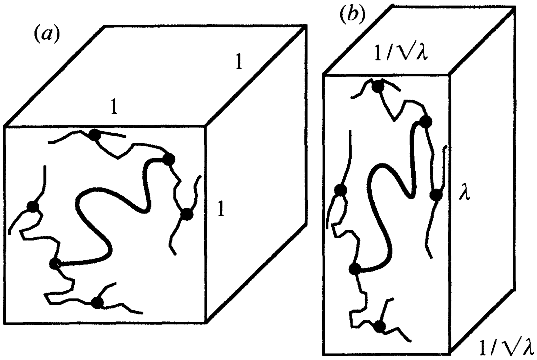

Figure 6. A block of rubber undergoing a distortion by factors of λ along the z direction and $1/\sqrt{\lambda}$ in the two perpendicular directions. Volume is thus conserved. A test strand (heavier line) is shown attached to neighbouring chains in the network. The average of the log of the probability of such a strand over its formation probability yields the elastic free energy.

The optimal λ derives from setting $\partial F_{\mathrm{el}}/\partial\lambda = 0$ and is $\lambda_{\mathrm{m}}(Q) = (l_z/l_{\mathrm{p}})^{\frac{1}{3}}$. It is a function of the nematic order Q which is as yet undetermined. For $Q > 0$ (a prolate phase $l_z > l_{\mathrm{p}}$) and hence $\lambda_{\mathrm{m}} > 1$. There is a spontaneous elongation of the sample on cooling to the nematic state. There is a flattening ($\lambda < 1$) for oblate case where $Q < 0$ (for the chain). In figure 6 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 $F(Q) = F_{\mathrm{nem}}(Q) + F_{\mathrm{el}}(\lambda_{\mathrm{m}}(Q), Q)$ where $F_{\mathrm{nem}}(Q)$ 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 and the constant density constraint means that chains on becoming nematic cannot adopt their natural nematic melt shape. The nematic–isotropic transition temperature for a crosslinked system, $T_{\mathrm{NI}}^{(x)}$, is thus lower than the melt value T_{NI}, see Warner *et al.* (1988) for theory and Mitchell & Davis (1993) for experiments.

Applying stress along the ordering direction (for rubbers crosslinked in the isotropic phase the applied stress defines the nematic direction) is akin to applying an E or B field to a simple nematic. Application to the isotropic phase can induce nematic order (if one is below the critical point). Inducing the nematic state discontinuously induces a change of chain shape and hence a discontinuous change in the shape of a sample, that is, the stress–strain relation is discontinuous. Stress applied to a system that is on the brink of ordering achieves a much higher and nonlinear response in, among other things, Q which determines the anisotropy of refractive index. Thus the stress-induced birefringence near T_{ni} rapidly increases, the nonlinearity being a deviation from the stress optical law, see experiments (Schätzle *et al.* 1990) and theory (Wang & Warner 1991).

Uniaxial compression initially presses chains to oblate ($Q < 0$), an ultimately unstable state for a system that would spontaneously form a prolate phase if cooled. At large enough compression along the z axis a nematic state is formed with its

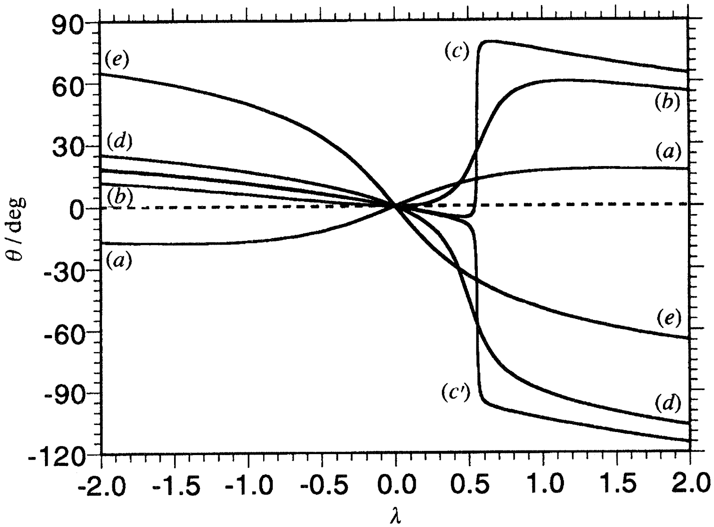

Figure 7. Instabilities in the director for a shear imposed on a monodomain nematic elastomer. Final director angle θ with respect to the initial director direction is plotted against the shear strain λ. Various angles α, the direction between the shearing direction and the initial director, label each θ–λ curve: (*a*) 0°, (*b*) 30°, (*c*) $37.2^{\circ -}$, (*c′*) $37.2^{\circ +}$, (*d*) 45°, (*e*) 90°. At a critical $\alpha = 37.2°$ there is a director jump at a critical λ.

largest principal axis in the x–y-plane. The applied stress makes the resultant state biaxial like a rugby ball pressed along one of its shorter axes. Bladon & Warner (1993) discuss this transition to a biaxial nematic rubber.

A rubber formed in a nematic melt has 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 $T_{\mathrm{NI}}^{(x)}$ is now greater than the melt value. Experiment (Mitchell & Davis 1993) and theory (Warner *et al.* 1988) agree qualitatively.

A nematic monodomain elastomer offers much richer possibilities not found in standard elasticity: there is a barrier (due to the network) to rotation of the director from its initial direction, $\boldsymbol{n}_0$. Monodomain elastomers 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 (Kupfer & Finkelmann 1991), a melt can be lightly crosslinked and then stretched by a mechanical field before a second crosslinking. The external stress creates a nematic monodomain if the sample is cooled below T_{ni}. 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 $\boldsymbol{n}_0$ and the strain axes the response is discontinuous; see figure 7. The jump over a barrier resembles that in the Frederiks transition in conventional nematics where instead fields are applied to the bulk and surface anchoring provides the barrier to director rotation. This elasticity where strain and internal rotation are coupled, where instabilities can occur and where stress and strain are discontinuously related as barriers to rotation are overcome, is apparently unique to these ‘solid liquid crystals’.

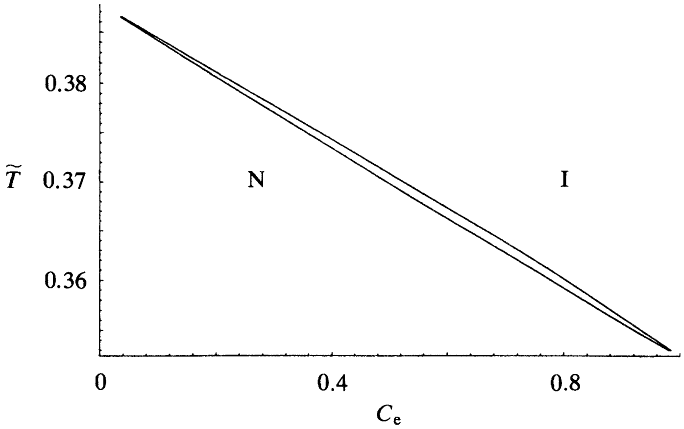

Figure 8. The biphasic region of a transesterifying main chain LCP. Reduced temperature is plotted against volume fraction of chain ends (itself proportional to the inverse mean chain length). At a volume fraction and temperature corresponding to a point inside the phase gap the polyester melt will fractionate into a longer chain nematic melt coexisting with a shorter chain isotropic melt.

(*e*) *Transesterification in nematic polymers*

Polyesters can break and reform at any of their ester linkages. If a pair of polymers are close at the time and are both broken, they can exchange material this way, thereby altering their molecular mass distribution while keeping the number of chain ends (and hence the number of chains) constant.

When the nematic energy per monomer depends on the length of the chain on which the monomer resides the ability to change chain length can couple in the nematic–isotropic equilibrium. This is what happens when a transesterifying system undergoes a phase transition. Worm-like and other non-freely jointed rod models of polymers indeed give a nematic free energy monomer that is dependent on chain length. The end regions of such chains have more freedom than regions deeper inside a chain, causing short chains to prefer the isotropic state. Thus in a melt at the N–I transition there is a partitioning of the fixed number of chain ends unequally between coexisting nematic and isotropic phases which received respectively fewer and more than average (the mean chain length is longer in the nematic phase). Biphasic N–I coexistence has been calculated with a worm model (Bladon *et al*. 1993) to occur over a finite temperature interval; see figure 8. This is one of the simplest examples of self-assembly (of a rather constrained type) being driven by a nematic field. Transesterifying nematic polymers have been studied by Arrighi *et al*. (1992) and Abis *et al*. (1993) who saw the neutron signal from a protonated/deuterated mixture fade as transesterification mixed up the initially P and D chain sequences. In some cases phase gaps too wide to be explained by transesterification undoubtedly arise. Systems with more than one type of monomer have compositional fluctuations, possible with transesterification, much greater than the $1/N$ effects discussed above (N being the chain length).

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