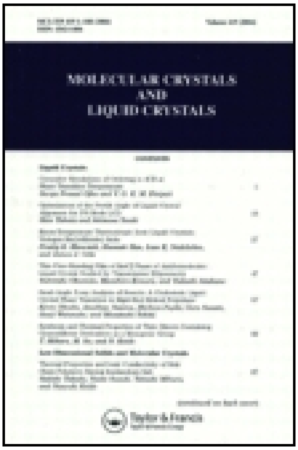

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Phases and Conformations Of Comb Polymer Liquid Crystals

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Phases and Conformations Of Comb Polymer Liquid Crystals

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Abstract Polymer entropy is antagonistic to nematic order. Comb polymer architecture forces nematic and flexible elements together in one phase. The result of this is predicted to be several new nematic phases. We show how this underlying principle of competition gives a description of complex phase diagrams. Results include phases with apparently negative order parameters, reentrancy, changes in chain conformation away from spherical and molecular defects. Two components require two order parameters - the theory is similar to that of two, coupled Maier-Saupe systems.

Introduction

Polymers add a new element to liquid crystal physics because they are generally entropy-driven. However their tendency to assume the most chaotic configurations is antagonistic to any nematic ordering requirements they might have. This interplay yields new possibilities which we outline below in discussing phase behaviour. The state of a chain is mirrored in its configurations. Hence we shall at the same time as discussing phases, discuss chain shape. Indeed this is the best way of microscopically understanding the new comb phases.

Nematic character has been given to polymers by concatenating stiff elements to give worm-like molecules, attaching rods to a flexible polymer back-bone to give the teeth of a comb and, additionally, by combining[1] stiffness in both the back-bone and teeth of a comb molecule. Attachment of teeth by hinges that are too stiff destroys nematic phases. In the nematic-forming phases a coupling between teeth and polymer back-bone was first seen by Koch *et al*[2] who looked at the stress-optical coefficients of nematic networks and found negative values. These became much more negative in the pretransitional region before the isotropic to nematic transition, suggesting (in the classification of Wang and Warner[3]) N_I or N_{II} tendancies. Biaxiality of the nematic phase of this system under strain suggested N_I, see figure 1:

Figure 1. Three possible phases for comb nematics.

If (S_A, S_B) are the order parameters of side chains (A) and main chain (B) then we have N_I with (+,-), N_{II} with (-,+) and N_{III} with (+,+). The length of teeth is $x\ell$ and their spacing along the backbone is $n\ell$ where ℓ is the chain diameter. The angle of the chain tangent vector at arc position s along the chain is $\theta(s)$ with respect to the director $\underline{n}$.

Microscopic evidence for coupling comes from neutron scattering[4,5] in a system dominated by side-chain ordering, where the back-bone polymer configurations in the N phase, instead of being the usual spherical Gaussian, are flattened to oblate spheroidal. The radius of gyration $<R^2>$ parallel to the director $\underline{n}$ was found to be smaller than that in the perpendicular plane.

Polymer Entropy and Nematic Ordering

A crude but accurate model for a polymer is to represent the bonds (steps) of a polymer as bonds on a lattice, see figure 2.

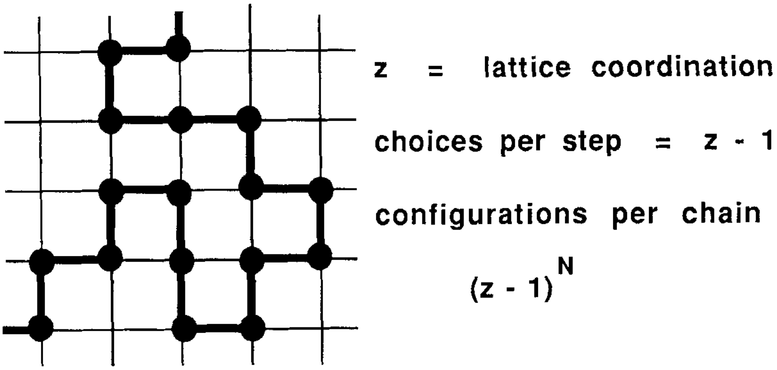

Figure 2. A lattice model for the entropy of a polymer.

Restrictions (nematic, smectic or mechanical) on chain entropy are fiercely resisted.

If the coordination number of the lattice is z, then there are z-1 choices of where to put each bond, slightly fewer than this if one considers excluded volume correlations. z might be 6 in 3-D and 4 in 2-D. The entropy $\mathcal{S}$ of a chain of N steps in 3-D and 2-D is $\mathcal{S}_3 \sim k_BN \ln(5)$ and $\mathcal{S}_2 \sim k_BN \ln(3)$ respectively. The reduction in entropy if a chain is confined toward a plane (an extreme case of an oblate chain is chosen for illustration) is $\Delta\mathcal{S} = \mathcal{S}_2 - \mathcal{S}_3 \sim -k_BN \ln(5/3)$, giving a substantial rise in the free energy, $\Delta F \sim k_B TN \ln(5/3)$. This rise in F resists the nematic ordering of the teeth, effecting phase equilibria and transitions. It is the reason[6] for the higher latent heats in polymeric liquid crystals - the polymer entropy reservoir participates. Confinement toward a plane was also seen in neutron scattering from smectics[4]. There it is proposed[7] that the entropy penalty of confinement is relieved by hopping between layers, that is by molecular defects.

If a polymer is stretched out toward being a rod by the nematic field, in this crude model $z-1 \sim 1$ and $\mathcal{L}_1 \sim 0$. The rise in free energy is even greater. de Gennes[7,8] has proposed "hair-pin" defects as a mechanism for entropy recovery. If a chain is stretched out mechanically the rise in the free energy is seen as an elastic resistance to distortion. The above entropy arguments show that the rise in F is proportional to T, whence the well-known result that the modulus of a rubber is given by the product of temperature and the number of chains crosslinked. This elastic contribution couples to the nematic free energy effecting transitions in nematic networks[8,9,10,11]. The picture of entropically elastic chains under tension from the nematic field is a good one to keep in mind when thinking of the differences between conventional and polymer liquid crystals.

The method of describing polymer configurations used in calculating free energies is more sophisticated than our crude model: worm-like chains must be taken since it is the tangent vector of the chain which couples to the nematic field. The worm chain in a nematic field has similarities with the rotational diffusor in a quadupolar potential and yields the spheroidal wave equation[12,13]. The stiffness of the chain is determined by the bend modulus ε which yields a persistence length for the chain ~ ε/T. This length compared to the chain dimension ℓ sets the entropy scale. We shall not go into the details here, if suffices that results for a worm nematic are qualitatively the same as for conventional nematics, that is there is a first order phase transition from isotropic to nematic.

For the nematic part of the problem we must consider two coupled influences: the teeth (A) interact nematically among themselves (v_A) and with the backbone (B) both nematically and via the hinges (together represented by v_m); the backbone interacts with itself (v_B) and with the teeth (v_m). If we denote the order parameters of the teeth and backbones by the averages $<\ldots>$, over P_2 as $S_A = <P_2(\cos\theta_A)>$ and $S_B = <P_2(\cos\theta(s))>$ respectively, then the mean field potentials U seen by teeth and back-bone are

$$U_A = \{ \chi\, v_A\, S_A + (1 - \chi)\, v_m\, S_B \}\, P_2(\cos\theta_A) \tag{1}$$

$$U_B = \int_0^L ds\, \{ (1 - \chi)\, v_B\, S_B + \chi\, v_m\, S_A \}\, P_2(\cos\theta(s)) \tag{2}$$

χ is the volume fraction of teeth and $(1-\chi)$ is that of back bone, $\chi = x/(x+n)$ with x and n the tooth length and spacings defined in figure 1. The sum over chain configurations $\theta(s)$, where θ is the angle of the tangent vector with the z axis at the arc point s along the chain, is more complicated than our lattice illustration above and is also more complicated than the sum required by the Maier-Saupe (M-S) theory for ordinary nematic rods with a potential such as (1). The results have qualitative similarities with the M-S theory - see reference 6 for an explicit solution in the prolate case and ref. 7 for a fuller explanation of the potentials (1) and (2) and their solution. In effect we have in (1) and (2) two, coupled M-S systems. The two-component M-S theory is a generalisation akin to the introduction of 2 sub-lattices in the extension of Curie-Weiß theory of magnetism to a theory of anti-ferromagnetism. We shall find that, depending on the choice of coupling constants, one or other component will dominate the ordering and that the other component will follow in a manner determined by the relative magnetude of the self coupling to the mutual coupling, v_m. The details of this process is best exposed by a discussion of some of the complex phase diagrams that can arise for comb polymers.

Competition between Nematic Phases.

We see that there are many nematic ordering influences. Rather than trying to estimate the magnetudes of the coupling constants directly, we shall asume some values in order to illustrate the complex possibilities for ordering.

The mutual coupling v_m between A-B is very important. It has two components: a nematic v_C driving A and B parallel and the hinge v_f making A and B perpendicular. As χ is varied at fixed side chain length x (by varying n), $v_m = v_C - v_f/x(1-\chi)$ changes, thereby altering the phase competition.

The self couplings v_A and v_B are such that if A and B were decoupled ($v_m = 0$), the components would order at temperatures $k_BT_A = .22\chi v_A$ and $k_BT_B = .38\sqrt{\{(1-\chi)v_B\varepsilon/\ell\}}$, the former being the result of M-S theory, the latter the solution of the polymer liquid crystal problem[6,12]. The component dominating the ordering is that with the greater of T_A or T_B, the sign of v_m determining which comb phase is exhibited.

If v_m is > 0 the two components want to be parallel and, since individually their ordering is naturally positive, there is no conflict and N_{III} results. This is so for $\chi < \chi_o$ in figure (3a). If v_m is < 0 ($\chi > \chi_o$ in figure (3a)), then A and B wish to be

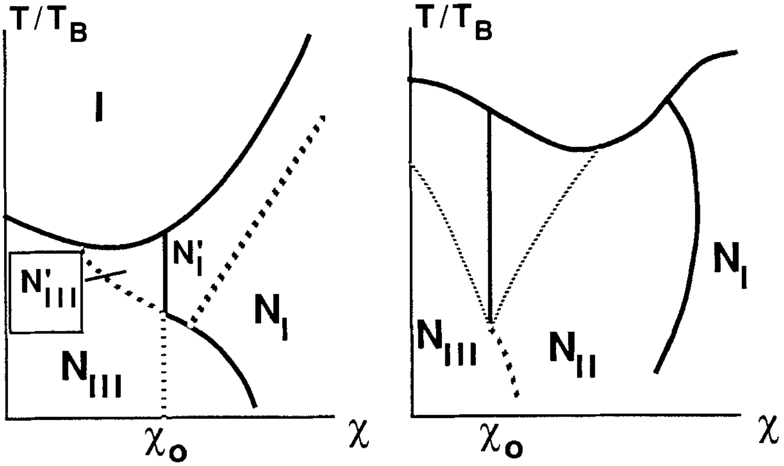

Figure 3. Phase diagrams for side chains of length x = 3. Temperature is reduced by the value at the N-I transition for pure main chain (B). Volume fraction χ of side chains is varied by varying their spacing n along the back bone. Coupling constants are in the ratio $v_A:v_B:v_C:v_f:\varepsilon/\ell$ (a) 3:2:2:3:2. (b) 1:2:1.2:3:2, note the reentrancy.

perpendicular, unless their own ordering is overwhelming. What happens depends on the relative sizes of the intrinsic ordering temperatures for the current χ, $T_A(\chi)$ and $T_B(\chi)$, and the current temperature T. Let us take the example of figure (3a). At $\chi = \chi_o$ we have $T_A(\chi) > T_B(\chi)$, the teeth order before the backbone and hence lowering T at constant χ ($> \chi_o$) yields the I to N_I transition at T around $T_A(\chi_o)$. It can be proven[14] that the N_{III}/N_I phase line is exactly vertical in this region. The N'_{III} and N'_I around χ_o are so denoted with primes because the B component, which naturally orders at lower temperatures, is only weakly ordered with $|S_B| \leq .17$. The teeth have already ordered (since $T < T_A(\chi_0)$) and impose an order (of the same sign as v_m) on B. It is as if the teeth were an external field inducing a para-nematic phase. It is known[15] that polymer liquid crystals in an external field are qualitatively the same as conventional nematics. This analogy, set up in ref. 3, is further explained in ref. 14 and is used to explore the region around P in the phase diagram.

As temperature is further lowered so $T \le T_B(\chi_0) << T_A(\chi_0)$, then the N_I phase for $\chi \le \chi_0$ is surplanted by the N_{III} phase - now the ordering of the backbone takes place and overcomes the negative effect of the hinge whence $S_A > 0$ and $S_B > 0$.

This interplay between the three couplings is further illustrated in fig. (3b). At χ_0 , where $v_m = 0$, the components are effectively decoupled and instead $T_B(\chi_0) > T_A(\chi_0)$. This means that the N_{III} phase from the $v_m > 0$ region meets an N_{II} phase from the $v_m < 0$ region where $T_B(\chi_0) > T > T_A(\chi_0)$, that is the backbone B orders first and the hinges drive the A component to be perpendicular with negative order parameter. Contrast this with fig.(3a) where the opposite is true and N_{III} results. As χ is increased, the role of the side chains grows until $T_A(\chi) \sim T_B(\chi)$, which occurs at χ'. Now the side chains can play a dominant role and the backbone must follow - N_{III} is the result. Because of quantitative differences between Maier-Saupe theory and that of nematic polymers (the spheroidal wave equation approach), in particular the difference in the temperature dependence of ordering, the N_{II}/N_I coexistence is predicted to be re-entrant. At χ fixed around χ', variation with T is predicted to yield the sequence $N_{II}/N_I/N_{II}/I$.

Another example is given in fig. (4a) where $v_m = 0$ at $\chi = 0$. It is the system of fig. (3a) but with v_c halved thus making the hinges dominant over the entire range of χ. N_{III} has now been eliminated, except perhaps in the low T, χ corner, in favour of the "perpendicular" phases N_{II} and N_I. For a wide range of values of χ it is predicted that, at fixed χ, varying T yields the phase sequence $N_{II}/N_I/I$. This involves the exchange in sign of the order parameters and is plotted in fig. (4b). If the dominant optical anisotropy were to occur in the side chains A, we would measure an increase in the apparent optical anisotropy of the liquid (possibly going from negative to positive) with *increasing* temperature, followed by a diminishment until the I phase is achieved and it vanishes altogether. This would represent an apparently anomolous sequence of orderings.

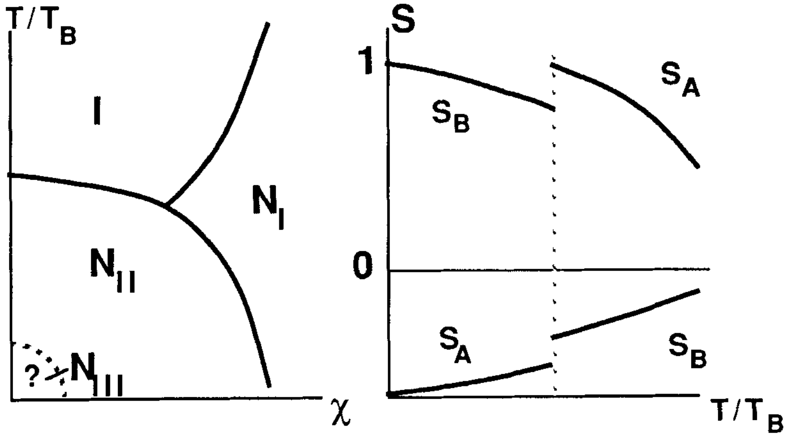

Figure 4. Negative Main Chain - Side Chain Coupling.
(a) Combs as in figure (3a) but the A-B nematic coupling v_C has been halved thus effectively eliminating N_{III}. T variation with χ fixed at 0.4 shows A and B exchanging roles as seen from the change in sign of their order parameters.

Conclusions

The antagonistic influences of polymer entropy and nematic ordering, when combined in one molecule, add a new twist to liquid crystal equilibria. Combs have two components, teeth and backbone, and hence two order parameters and greater possibilities for new phases. We predict several novel transitions and it is hoped that experiments, already having found the coupling of main chains to the nematic order of the teeth, will continue and test our predictions. The "combined" phases offer the widest range of possibilities and scattering offers the most direct microscopic test. Networks of more exotic phases, including smectics, may offer new scope for both theory and experiment.

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