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Self-Assembly in Living Nematics

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ABSTRACT: New nematic materials have been synthesized that use hydrogen bonding as a mechanism for self-assembly. These materials are "living" systems, their bonding properties determined by subtle interactions. Models of two systems, a living low molecular weight nematic and a living polymer liquid crystal are constructed. Nematic effects provide significant enhancement to bonding, giving rise to discontinuous jumps in concentration variables at the nematic–isotropic transition.

1. Introduction

Hydrogen bonding between dissimilar molecules has been suggested as a mechanism for the construction of mesogenic molecules.[1] Hydrogen bonds between pyridine and carboxylic acid have been used to form complexes of side chain polymer liiquid crystals (PLC's),[1] small molecule liquid crystals[2,3] and extended chain PLC's.[3] Hydrogen bonding has also been used to assemble nonnematic polymer molecules.[4]

Due to the weak nature of the H bond (compared to that of a covalent bond), molecules formed by hydrogen bonding rapidly break and recombine at melt temperatures. For the case of a side chain PLC with hydrogen bonding units at the end of each side chain, this leads to the formation of a transient network. A main chain PLC polymerized using H bonds will be polydisperse, and a low molecular weight liquid crystal assembled by hydrogen bonding from smaller fragments will have different populations of each of the constituent fragments, both bound and unbound. The amount of bonding in all of these systems is very temperature dependent. The relative weakness of the hydrogen bonding in these systems allows other interactions, *e.g.* the nematic interaction, to play a large part in the self-assembly and resulting physical properties.

In this paper the effect of the nematic interactions on bonding will be considered for the case of self-assembling small molecule liquid crystals and main chain PLC's. The equilibrium length distribution for PLC's and the populations of assembled and unassembled molecules in low molecular weight liquid crystals will be calculated for simplified models. Simple models are needed for these systems that retain the essential physics; the competition between rotational and translational entropy, hydrogen bonding energy, and nematic interactions. Bond formation directly lowers the energy but also alters the number of molecules and hence the free energy via a loss of both translational and rotational entropy. The formation of a molecule with different nematicity will also effect the free energy. The competition between these effects and the effect on the amount of self-assembly is examined in this paper. In section 2.1 low molecular weight liquid crystals will be discussed. The assumptions needed to model these newly synthesized compounds which form self-assembling or "living nematics" are outlined and a minimum theory which captures the essential physics is developed. In section 2.2 the theory for self-assembling "living PLC's" is developed. The self-assembling PLC's discussed in this paper have close parallels with self-assembling worklike surfactant micelles when the PLC's are in the isotropic phase.[5] In sections 3.1 and 3.2 numerical results for living nematics and PLC's are presented, and conclusions are made in section 4.

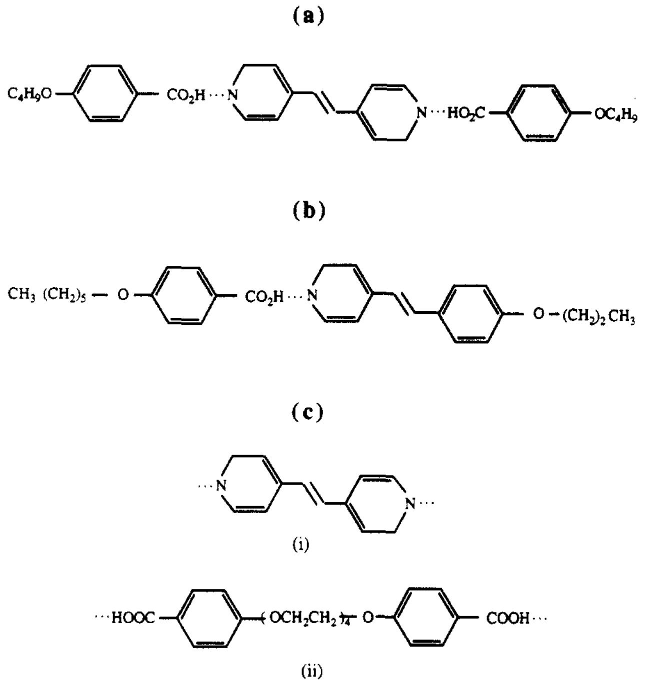

Figure 1. Typical compounds that form hydrogen bonded "living" nematics. (a) A typical nematic forming molecule described in ref 3 first forms a nematic phase at 166.5 °C and becomes isotropic at 178.6 °C. (b) The compound 60BA-30Sz described in ref 2 has only one hydrogen bond and becomes nematic at 140 °C and isotropic at 162 °C. (c) A typical compound forms living nematic polymer chains, via the hydrogen bonding of the two components, (i) containing the pyridines and (ii) containing the carboxylic acid. The nematic phase is formed at 168.5 °C and becomes isotropic at 180 °C.

2.1. Low Molecular Weight Liquid Crystals

A typical hydrogen bonded small molecule liquid crystal which forms smectic-A and nematic phases is shown in Figure 1a.[3] The transition temperatures are as follows: crystalline → smectic-A = 148 °C, smectic-A → nematic = 166.5 °C, nematic → isotropic = 178.6 °C. Other molecules that have been studied include a complex

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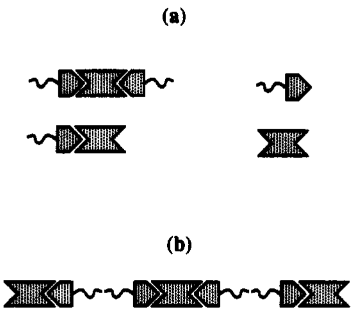

Figure 2. Schematic representation of the component molecules in the melt. (a) The molecule in Figure 1a can form four different subspecies in the melt, the populations of which depend on temperature, the strength of the hydrogen bond, and subtle nematic effects. (b) The polymeric molecule described in Figure 1c above forms polymers via hydrogen bonding.

denoted by 6OBA-3OSz, shown in Figure 1b,[2] which again has nematic and smectic-A phases: crystalline → smectic-A = 102 °C, smectic-A → nematic = 130 °C, nematic → isotropic = 155 °C. The possible combinations of the four possible constituent molecules for the first compound are shown schematically in Figure 2a. In a melt there will be different populations of each of the four possible combinations of the constituent molecules, and it is the purpose of this paper to find out how the competitive influences, particularly nematic effects, alter the concentrations of each component.

The system could be modeled as in Figure 2a, as four different species in equilibrium which can bond together, hence altering the free energy and concentration of each fragment. Using a Maier-Saupe mean field model the nematic interaction of each species with the other species would be different, and a different strength nematic interaction parameter for each of the intermolecular interactions would require a total of ten different parameters. A simplified model for the system is needed which retains the essential competition between entropy, bonding energy, and nematic energy but reduces the number of parameters needed. A convenient simplifying assumption is that the system consists of one type of molecule (referred to as a "monomer") that can hydrogen bond together to form a molecule twice as long (referred to as a "dimer"). In ref 2, a complex was formed from the acid part of the molecule shown in Figure 1b, which had behavior qualitatively similar to the complexes formed from both of the different molecules. We hope to be able to describe both sorts of systems qualitatively with our model. As some of the chemical systems are two component, biphasic transitions are allowed. In experiments no biphase is seen (or the biphase width is very small). By considering a one component system the possibility of biphases being formed is neglected, but the effect of the multicomponent nature of the system on the properties that will be calculated will be small.

In the model the monomers are denoted by a "1" subscript, dimers by a "2" subscript. For convenience the molecules are imagined to be inscribed on a lattice of N sites of volume v. The molecules are assumed to be noninteracting, except via the nematic mean field Q. Hence the translational entropy of each species i of n_i molecules is given by an ideal gas term:

$$-\frac{S}{k_{\mathrm{B}}} = n_i \ln \frac{n_i}{N} \equiv N\mathrm{v}c_i \ln c_i - c_i \ln \mathrm{v} \tag{1}$$

The quantity c_i is hence the concentation of species i. Setting the volume v of a lattice site equal to 1, the free energy density, per lattice site in units of $k_{\mathrm{B}}T$, can be written as

$$F = \sum_{i=1}^{2}[c_i \ln c_i + c_i f_i] + c_1 \frac{\beta E}{2} \tag{2}$$

The quantity βE is the energy of a hydrogen bond in dimensionless units ($\beta = 1/k_{\mathrm{B}}T$ is the normal inverse temperature). Since it takes two monomers to form each hydrogen bond, only half of this energy can be associated with each unbound monomer. The nematic free energy per monomer for each species is denoted by f_i, which is written in units of $k_{\mathrm{B}}T$ for convenience. The concentrations c_1 and c_2 will be chosen to minimize the free energy subject to the constraint that the total volume of material be fixed:

$$c_1 + 2c_2 = 1 \tag{3}$$

One sees that the maximum concentration of species i is $1/i$. The rods are assumed to interact via a Maier-Saupe-like mean field Q, and furthermore it is assumed that a bound pair behaves like a stiff rod. This assumption overcomes the considerable difficulties of accounting for "real" dimers which have internal degrees of freedom such as flexibility.[6,7] A more realistic model might be that each molecule interacts with the mean field Q with arbitrary strengths, chosen so that, say, the monomer could interact much more weakly than the dimer. We take each rod to have a nematic interaction v with the mean field Q proportional to the rod's length. The Maier-Saupe interaction potential U_i is therefore:

$$U_i = -ivQP_2(u) \equiv -ivQ\frac{1}{2}(3u^2 - 1) \tag{4}$$

where $u = \cos\theta$; θ is the angle the molecule's long axis makes with the director, conventionally chosen to be the z axis; P_2 is the second Legendre polynomial. The free energy per rod is therefore

$$f_i = -\ln Z_i - \frac{1}{2}\beta\langle U_i\rangle$$
$$Z = 2\pi\int_{-1}^{1}\mathrm{d}u\ e^{ivQP_2(u)} \tag{5}$$

where the extra term ($\langle U_i\rangle$) arises from the need to eliminate the double counting introduced by the mean field.

Each individual species has an order parameter Q_i which contributes to the total order parameter Q in the following way:

$$Q = \frac{\sum_i ic_iQ_i}{\sum_i ic_i} \tag{6}$$

When $\langle U_i\rangle = -viQQ_i$ where $Q_i = \langle P_2(u)\rangle_i$, the i subscript denoting an average over the i component probability distribution, the free energy is

$$F = \sum_{i=1}^{2} c_i[\ln c_i - \ln Z_i] + c_1\frac{\beta E}{2} + \frac{\beta v}{2}Q^2 \tag{7}$$

The sum of the two mean field terms has been combined to give the $\beta vQ^2/2$ term.

The Q_i's and hence Q must be chosen to minimize the free energy:

$$\frac{\partial F}{\partial Q_i} = \frac{\partial Q}{\partial Q_i}\frac{\partial}{\partial Q}\left[-c_1 \ln Z_1 - c_2 \ln Z_2 + \frac{\beta v}{2}Q^2\right] = 0$$

$$\Rightarrow Q = \frac{c_1}{Z_1}\int_{-1}^{1}\mathrm{d}u\, P_2(u)\, \mathrm{e}^{\beta v Q P_2(u)} + \frac{2c_2}{Z_2}\int_{-1}^{1}\mathrm{d}u\, P_2(u)\, \mathrm{e}^{2\beta v Q P_2(u)} \tag{8}$$

Identifying the first integral as $Q_1 = \langle P_2(u)\rangle_1$ and $Q_2 = \langle P_2(u)\rangle_2$, recover eq 6 for Q; i.e. the theory is self-consistent. Equation 8 is the analogue of the normal self-consistency equation for the Maier-Saupe theory for the two component case. Since Q is implicitly a function of c_1 and c_2, an equation determining the dependence of the c_i's on Q must be obtained in order to solve (8) for Q.

Taking the derivative of (7) with respect to c_1 after substituting for c_2 yields the following:

$$\frac{\partial F}{\partial c_1} = \frac{1}{2} + \ln\left[\frac{c_1}{\sqrt{\frac{1}{2}(1 - c_1)}}\right] + \frac{\beta E}{2} - \ln\left[\frac{Z_1}{\sqrt{Z_2}}\right] + \frac{\partial Q}{\partial c_1}\frac{\partial}{\partial Q}\left[-c_1 \ln Z_1 - c_2 \ln Z_2 + \frac{\beta v}{2}Q^2\right] = 0 \tag{9}$$

The derivative with respect to Q is zero from (8). Rearranging to obtain a quadratic for c_1 and solving (taking the solution giving positive c_1), one obtains

$$c_1 = \frac{A}{2}[\sqrt{1 + 4/A} - 1] \tag{10}$$

where

$$A = \frac{Z_1^2}{2Z_2}\mathrm{e}^{-(\beta E + 1)} \tag{11}$$

By substitution of this expression for c_1 into (8) it is a simple numerical procedure to solve for Q self-consistently. When $Q = 0$, $Z_1 = Z_2 = 4\pi$, giving $S_{\mathrm{rot}} = k_{\mathrm{B}} \ln 4\pi$, the rotational entropy of a rod. If we set $E = 0$ in the above two expressions, the limit where two molecules can join together without gaining any energy, we obtain $c_1 \approx 0.75$ and $c_2 \approx 0.25$. The system can gain mixing entropy by creating new particles, which balances the loss of translational and rotational entropy arising from destroying the two particles and only creating one.

2.2. Polymer Liquid Crystals

A typical molecule that can self-assemble into a long chain PLC is shown in Figure 1c.[3] The transition temperatures are as follows: crystalline → nematic = 168.5 °C, nematic → isotropic = 180 °C. The constituent molecules can self-assemble to form a polymer, shown schematically in Figure 2b. Again the simplifying assumption that the system is one component is made.

The system is allowed to have a distribution of chain lengths, with c_i denoting the number of chains of length i as before. These chains are inscribed on the same lattice of N sites of volume v. Each chain has two ends which are capable of forming hydrogen bonds. The energy that the chain will gain through making each of these bonds is half the energy of each hydrogen bond. Therefore each chain has an extra term in the free energy like $c_i\beta E$ (*cf.* the energy of half a hydrogen bond for each monomer in the free energy). The free energy density in units of $k_{\mathrm{B}}T$ per lattice site is

$$F = \sum_{i=1}^{\infty} c_i\,[\ln c_i + \beta E + if_i] \tag{12}$$

The quantity f_i is the nematic free energy per lattice site of a chain length i units.

A wormlike chain model is used for the nematic free energy of a polymer chain. The worm chain in a nematic field has been reduced to a spheroidal wave equation by the number of authors,[8-12] and the reader is referred to these references for a fuller description of the model. Only the main result will be presented here. A wormlike chain is represented by a continuous curve which is stiff (ϵ denotes the stiffness constant that governs the energy penalty for bending) and locally inextensible. Nematic effects are included via a Maier-Saupe mean field Q which is dependent on the orientation of the chain in space. The free energy per chain is

$$\frac{F_{\mathrm{chain}}}{k_{\mathrm{B}}T} = \lambda_0 \frac{L}{l_0} - \ln[\int \mathrm{d}\mathbf{u}\, Sp_n(\mathbf{u})]^2 + \frac{1}{2}\beta v Q^2 L \tag{13}$$

The quantity λ_0 is the lowest eigenvalue of the diffusion equation; $Sp_0(\mathbf{u})$ is the corresponding normalized wavefunction. Both are of course dependent on the nematic order Q and the temperature. $l_0 = 2\beta\epsilon$ is the inverse diffusion constant of the chain tangent vector $\mathbf{u}$ on the surface of the (θ,ϕ) sphere, describing the chain in the absence of nematic fields. The last term is introduced to eliminate the double counting introduced by the mean field as before; ν is the strength of the nematic interaction per unit length; L is the total arc length of the chain.

If the chain is infinitely long, the free energy reduces to the terms extensive in L (as the partition function becomes dominated by the first term in a series of terms weighted by $\exp(-\lambda_n L/l_0)$). This long chain limit is analogous to ground state dominance in a quantum mechanical system at long times. In this limit there is a nematic–isotropic phase transition at a reduced temperature of $\tilde{T}_{\mathrm{NI}} = k_{\mathrm{B}}T_{\mathrm{NI}}/\sqrt{v\epsilon} = 0.38775$. Adding the log term is the lowest order correction to account for the presence of chain ends. Higher terms could be considered, but these are exponentially smaller i the chain is at least one persistence length long.[13] Thus the log term in the free energy could be considered to be the free energy of a pair of chain "ends" due to the nematic field. It arises due to the extra freedom the chains enjoy. In future the term will be denoted by E_Q, the Q as a reminder of the Q dependence of the quantity. It is this term which will drive the system to alter its length distribution in a nematic field. Other models, *e.g.*, the freely jointed rod model, only have a free energy per segment length (or persistence length), as neighboring segments are uncorrelated, and hence the freely jointed rod model would not show any alteration of chain distribution in the presence of a nematic field.

To convert to a free energy per lattice site, the chain length measured in persistence lengths must be converted to a number of monomer lengths, since it is assumed that each monomer occupies one lattice site. If the monomer size is taken to be a, then

$$\frac{L}{l_0} = \frac{ai}{l_0} = \frac{i}{C_\infty} \tag{14}$$

where $C_\infty = l_0 a$ is Flory's C_∞ parameter. Henceforth the monomer volume will be set to v, the lattice size, and we will assume $C_\infty = 1$; *i.e.* the persistence length is equal to the monomer length. The order parameter for a distribution of chain lengths is defined in the same way as before—see (6). The free energy per lattice site of the *i*th species reduced by k_BT can be written

$$f_i = \frac{1}{C_\infty}\left[\lambda_0 + \frac{QQ_i}{\tilde{T}^2}\right] - \frac{E_Q}{i} \tag{15}$$

Inserting (15) into (12) and using (6) give free energy as

$$F = \sum_i c_i\left[\ln c_i + (\beta E - E_Q) + i\frac{\lambda_0}{C_\infty}\right] + \frac{1}{C_\infty}\frac{Q^2}{\tilde{T}^2} \tag{16}$$

The equilibrium length distribution c_i should minimize the free energy subject to the constraint that the total volume of material is fixed:

$$\sum_i ic_i = 1 \tag{17}$$

The free energy also has to be minimized with respect to the order parameters Q_i. This gives

$$\frac{\partial F}{\partial Q_i} = \frac{\partial Q}{\partial Q_i}\frac{\partial}{\partial Q}\left[\sum_i c_i\left(i\frac{\lambda_0}{C_\infty} - E_Q\right) + \frac{1}{C_\infty}\frac{Q^2}{\tilde{T}^2}\right] = 0 \tag{18}$$

Differentiating (16) now with respect to c_i, after applying the constraint as a Lagrange multiplier μ, one obtains

$$1 + \ln c_i + i\frac{\lambda_0}{C_\infty} + \beta E - E_Q + \mu i + \frac{\partial Q}{\partial c_i}\frac{\partial}{\partial Q}[\sum_i c_i(...)] = 0 \tag{19}$$

where the last term is zero using (18). Rearranging (19) gives

$$c_i = e^A e^{-Bi} \tag{20}$$

where $A = E_Q - \beta E - 1$ and $B = \mu + \lambda_0/C_\infty$. Using the constraint (17) and performing the sums as integrals yield the following

$$\bar{L} = \frac{\sum_{i=1}^{\infty} ic_i}{\sum_{i=1}^{\infty} c_i} = e^{(\beta E - E_Q + 1)/2}$$

$$c_i = \frac{1}{\bar{L}^2}e^{-i/\bar{L}} \tag{21}$$

The quantity $\bar{L}$ is the average chain length of the distribution measured in units of *i*. Alternatively, the average chain concentration $C = 1/\bar{L}$ can be used as a convenient parameter. On substituting the distribution (21) back into the free energy, one obtains

$$F = C\ln C - C + C(\beta E - E_Q) + \frac{1}{C_\infty}\left[\lambda_0 + \frac{Q^2}{\tilde{T}^2}\right] \tag{22}$$

The above free energy is very simple but is only valid at self-consistency (as it was assumed that $\partial F/\partial Q = 0$). It turns out that the minimization of (22) with respect to *Q* is stable, allowing a simple numerical minimization to find *Q*.

3. Results

3.1. Living Nematic Dimers. Upon examination of eq 9, the free energy for the dimer system, the relative concentration of the two species is determined by the translational entropy, the rotational entropy, and the nematic and bonding energies. Under the assumption that *Q* has been solved self-consistently, the quantity that determines the relative concentration of particles 1 and 2 is the term in the free energy linear in c_1

$$c_1\left[\frac{\beta E}{2} - \ln\frac{Z_1}{\sqrt{Z_2}}\right] \tag{23}$$

The term in brackets can be considered to be an effective chemical potential which sets c_1. At the phase transition point, the value of $Z_1/\sqrt{Z_2}$ is different for the nematic and isotropic phases. Hence there is a jump in the concentrations of each species at the nematic–isotropic transition.

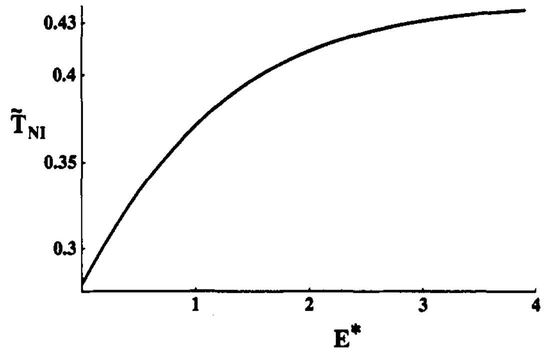

Figure 3. Variation of $\tilde{T}_{NI}$ vs E^*. The quantity of $E^* = E/\upsilon$ is the dimensionless strength of the hydrogen bond for the dimer. It can be related to *E* via υ, itself calculated from matching the experimental nematic–isotropic phase transition temperature to the dimensionless nematic–isotropic transition temperature of the theory, $\tilde{T}_{NI}$.

The critical parameter determining the behavior of the system is *E*, the energy of a hydrogen bond. The size of *E* compared to the nematic energy scale will determine if nematic effects are significant. In order to make calculations using the model outlined above, a reduced energy scale $E^* = E/\upsilon$ must be used so that $E/k_BT = E^*/\tilde{T}$. It is possible to calculate υ by matching the experimental phase transition temperature T_{NI} = 178 °C, e.g., to the phase transition temperature $\tilde{T}_{NI}$ predicted by the model. Therefore $\upsilon = k_B(178 + 273)/\tilde{T}_{NI}$. A problem arises as $\tilde{T}_{NI}$ is dependent on E^*. To proceed, E^* must be chosen and $\tilde{T}_{NI}$ calculated, allowing υ and hence *E* to be calculated.

The energy of a hydrogen bond in water is 20 kJ/mol, and this will be used as an estimate of the order of magnitude for a reasonable estimate of *E* (20 kJ/mol ≈ $5k_BT$ at T = 178 °C). Nematic effects on the behavior of the system will be investigated when *E* is of this order of magnitude.

Figure 3 shows how $\tilde{T}_{NI}$ varies with E^*, allowing *E* to be determined from $\tilde{T}_{NI}$. Figure 4 shows the concentrations of c_1 and c_2 at the transition temperature vs *E* in units of kJ/mol. The solid lines show the values in the nematic phase, the dotted lines show values in the isotropic phase. The jump in c_1 and c_2 at the transition is the difference between these two lines. Notice that as *E* dominates it forces the system to consist almost entirely of dimers, *i.e.* $c_2 \rightarrow 1/2$. It is possible to measure the amount of bonding in an experimental system by measuring the IR absorption intensity of the carbonyl bond in the carboxylic acid group on one of the dimer constituents. The absorption frequency changes due to the formation of a neighboring H bond. The intensity of this absorption band should be proportional to the total number of hydrogen bonds in the system and hence proportional to

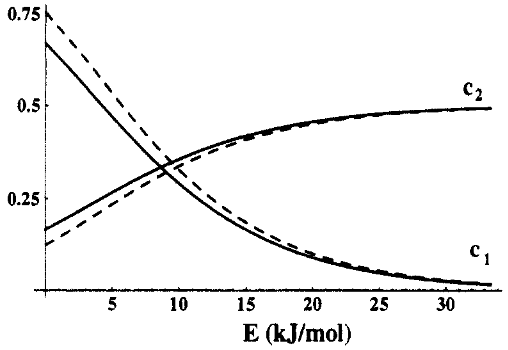

Figure 4. Concentrations of molecules 1 and 2 at the transition shown vs E, given in units of kJ/mol. The strength of a hydrogen bond in water is $\approx$ 20 kJ/mol. The dashed lines show the concentrations in the isotropic phase; the full lines, the concentration in the nematic phase. The difference between the two lines is the discontinuous jump in the concentrations of the two components at the transition.

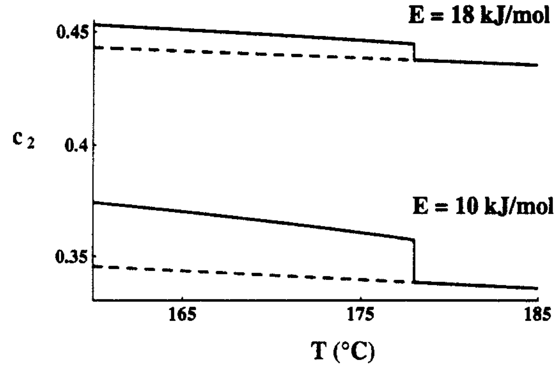

Figure 5. Concentration of the dimer c_2 shown vs T, with the phase transition set to 178.6 °C. The upper lines are for a bond strength E of 18 kJ/mol; the lower, for 10 kJ/mol. The dashed lines show the values of c_2 in the isotropic phase for comparison.

c_2. Experiments on the IR spectrum at a range of temperatures encompassing the crystal → nematic → isotropic region show a change in the IR intensity of the carbonyl bond at the NI transition, qualitatively confirming the predictions of our model.[2] Quantitative experimental results do not yet exist.

The jumps in c_2 at the transition temperature thus give an unambiguous indication that the nematic effect has a significant effect on the bonding of the system. However, the effect of the nematic interaction is smallest at the transition, and deeper in the nematic phase the effects will be larger, although more difficult to detect in an experiment.

Figure 5 shows how c_2 varies with temperature for two different values of E. The dashed lines show the equivalent system with no nematic interaction present. It is immediately obvious that the nematic interaction increases the stabilization of the c_2 component and grows with decreasing temperature; *i.e.* there is an effective extra "bonding" energy due to the nematic interaction.

Figure 6 shows the order parameters Q, Q_1, and Q_2 vs T for the same values of E as above. The order parameter for the monomers is smaller than for the dimers, as expected. Due to the approximations made in this model, *i.e.* the assumption of a simple form for the translational entropy, the assumption that the interaction of a "dimer" with the nematic field is twice that of a monomer, and not least the assumption that the real situation can be modeled as a monomer–dimer system, the size of nematic interactions on the bonding estimated above are only crude *estimates*, and depend very particularly on the assumptions made, particularly on the relative size of the nematic interaction. It is an experimental observation that the unassembled monomers cannot form a nematic phase on their own; it is the action of joining together to form a longer molecule that allows a nematic phase to be formed. In the model outlined above, both monomers and dimers are capable of forming nematic phases, although the transition temperature of the monomer alone is $k_B T_{NI}^{monomer} \approx 0.22\upsilon$—the normal phase transition temperature for a Maier-Saupe melt of rods. From Figure 3 we see that the combined system has a phase transition for high E^* of $\approx 0.44\upsilon$. Hence we are in the region where the nematic phase of the monomers is induced by the nematic phase of the dimers and the monomer order is therefore *paranematic*. If the monomers alone do not experimentally form a mesophase, this may be because the material crystallizes before a nematic state is obtained.

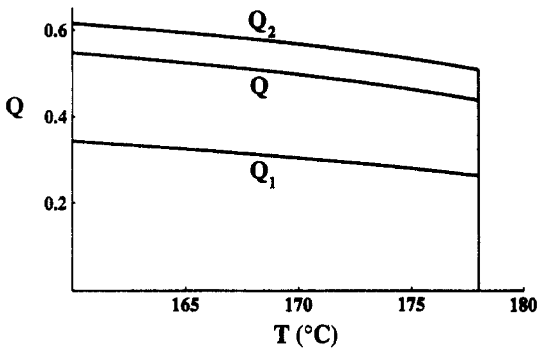

Figure 6. Order parameters Q, Q_1, and Q_2 vs T for E = 18 kJ/mol. The nematic–isotropic phase transition temperature has been set to T_{NI} = 178.6 °C. Notice how $Q_1 < Q < Q_2$. The transition in Q_2 induces Q_1 to be non-zero.

It would be possible to incorporate into a different model a much smaller nematic interaction between monomers than between dimers, as might be the case experimentally. This would mean the partition function Z_1 would be very much smaller than that of the above model, and consequently much larger jumps in c_1 and c_2 would be expected for such a model. Thus it might be expected that the effects outlined above are a lower bound to the nematic effects in real systems.

3.2. Living PLC's. As in the dimer case the nematic interaction in self-assembling hydrogen bonded chains increases the effective bonding interaction. The amount of extra bonding induced by the nematic field is dependent upon Q, and hence T.

In the wormlike chain model of a nematic polymer, the term in the free energy due to the chain ends acts as a chemical potential controlling the concentration of each species of chain. Again a reduced energy scale must be introduced. Keeping the previous notation, we define $E^* = E/\sqrt{\upsilon\epsilon}$. The value of E is calculated from the corresponding E^* in the same manner as before (that is, set E^*, match $\tilde{T}_{NI}$ to T_{NI}, calculate $\sqrt{\upsilon\epsilon}$ and hence E). For values of E^* equal to 1 and 2, the graph of E_Q vs T is shown in Figure 7. The quantity E_Q is negative, and thus the overall contribution to the free energy is positive; E_Q therefore promotes chain growth through penalizing configurations with many small chains (and hence many "ends"). Notice how E_Q is relatively unaffected by E^* away from the transition point. This means that the *relative* increase in $\bar{L}$ due to the nematic interaction away from the transition is almost independent of E^*.

There is a discontinuous jump in E_Q at the N–I transition, resulting in a jump in the value of average chain concentration or average chain length (remember $C = 1/\bar{L}$). The size of this jump is dependent on E in a complicated

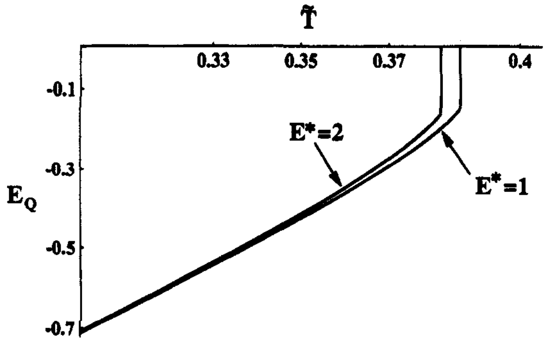

Figure 7. "End" energy E_Q vs $\tilde{T}$ for the living nematic polymer. The quantity E_Q is negative, promoting chain growth by adding an effective nematic bonding energy in addition to the hydrogen bond energy.

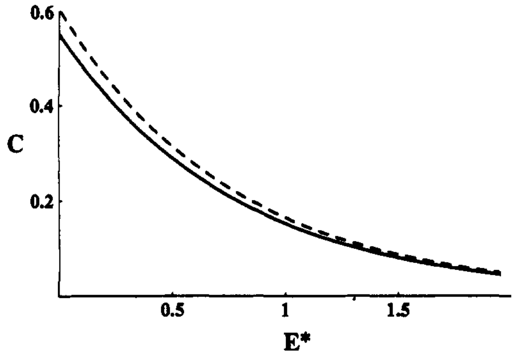

Figure 8. Average chain concentration of polymer chains C vs E^* at the nematic–isotropic transition point. The full line is the average chain concentration in the nematic phase, and the dashed line that in the isotropic phase. The difference between the two gives the jump in C at the nematic–isotropic phase transition.

way. Plotting C vs E (Figure 8) shows this dependence. The jump in the average chain length at the transition is small, due to the nematic effects being relatively weak at the transition, but on lowering the temperature, the nematic effect increases, leading to a significant increase in $\bar{L}$ over that obtained for the case where there is no nematic interaction. In Figure 9 $\bar{L}$ vs $\tilde{T}$ is shown for E equal to 12 and 25 kJ/mol, the dashed lines showing the system with no nematic interaction, the full lines the nematic PLC.

Again the easiest way to see the nematic effect is at the transition, which could be seen by the change in IR intensity of a bond related to the H bond. It is simple to calculate the concentration of H bonds per site C_H as

$$C_H = 1 - e^{E_Q - \beta E - 1} \qquad (24)$$

Figure 10 shows the predicted variation in IR intensity for the two values of E shown above and shows the predicted drop in IR intensity at the transition, again with the dashed lines describing an equivalent system with no nematic interaction.

4. Discussion

Using the wormlike chain model for PLC's and a Maier-Saupe model for small molecule nematics it has been shown that nematic interactions can play a vital part in the self-assembly of living nematic molecules, increasing the effective interaction strength of the bonding between the molecules. Although simple mean field models have been used, the models capture the essential physics, balancing the competition between translational, rotational, bonding, and nematic order. The choice of model for nematic interaction is important for correctly describing the experimental situation. Indeed, using a freely jointed rod

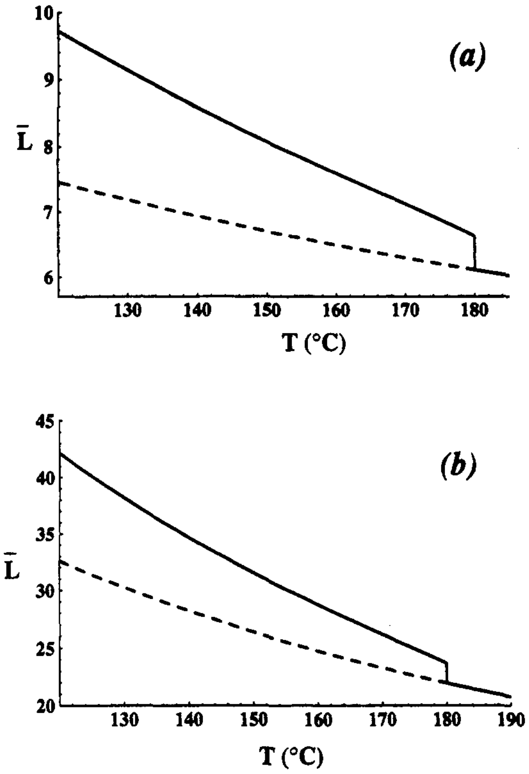

Figure 9. Average chain length of the polymer length distribution $\bar{L}$ vs T for (a) E = 12.5 and (b) E = 25 kJ/mol. The full lines are the nematic phase; the dashed lines, the isotropic phase for the equivalent system with no nematic interaction. The jump $\bar{L}$ at the nematic–isotropic transition can clearly be seen. The promotion in chain length over the equivalent nonnematic system is significant at low temperatures.

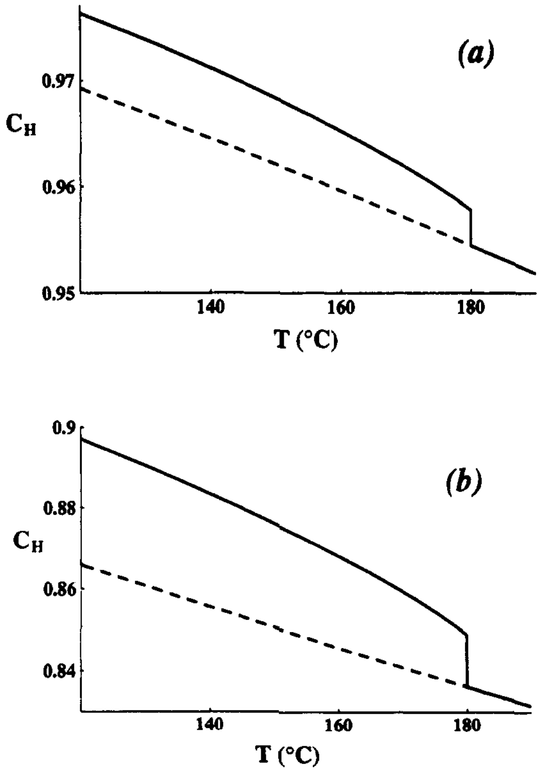

Figure 10. Concentration C_H of hydrogen bonds vs T for the polymer system for (a) E = 12.5 and (b) E = 25 kJ/mol, respectively. C_H should be proportional to the intensity of an IR band present in the nematic phase of the molecule (*i.e.* the H bond, if it can be experimentally measured).

model for the nematic interaction of the polymer would result in no subtle effects being predicted.

The polymeric properties of self-assembling PLC's described are difficult to observe, because they can only exist in melt phases. This prevents solution light scattering and GPC techniques from being used to determine molecular weight. Since the relaxation time of the molecules is very fast, due to the rapid breaking and recombination of chains, the normal viscoelastic properties characteristic of polymer melts will not be observed unless very high frequency measurements are made. In the current absence of these measurements, the predictions in this paper of jumps in IR intensity at T_{NI} may provide the only direct evidence for association into extended structures, as this effect arises from the connectivity of the chain.

The mechanism of hydrogen bonding forms PLC's with nematic phases, with dynamics that are very different from normal immutable PLC's. The formation of nematic phases should be a very fast process, as any steric hindrances to forming an ordered phase can be avoided by simply breaking and reforming the chain. Also the mechanism might be used to obtain nematic PLC's with very long average chain lengths (typical polyester PLC's have chain lengths of only, e.g., 10–20 units[14]). The dynamics of self-assembling polymers have been extensively discussed for isotropic phases,[5] but the generalization to nematic phases is a nontrivial problem that nonetheless should provide revealing insights into the formation of ordered phases by a self-assembling mechanism.

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References and Notes

(1) Kato, T.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1989**, *111*, 8533.
(2) Kato, T.; Uryu, T.; Kaneuchi, F.; Chihiro, J.; Fréchet, J. M. J. *Liq. Cryst.* **1993**, *14*, 1311.
(3) Alexander, C.; Jariwala, C. P.; Lee, C. M.; Griffin, A. C. Preprint.
(4) Hilger, C.; Stadler, R. *Makromol. Chem.* **1991**, *192*, 805.
(5) Cates, M. E.; Candau, S. J. *J. Phys.: Condens. Matter* **1990**, *2*, 6869.
(6) Heaton, N. J.; Luckhurst, G. R. *Mol. Phys.* **1989**, *66*, 65. Photinos, D. J.; Samulski, E. T.; Toriumi, H. *J. Chem. Phys.* **1990**, *97*, 2758. Photinos, D. J.; Samulski, E. T.; Toriumi, H. *J. Chem. Phys.* **1990**, *97*, 7688.
(7) Terentjev, E.; Petschek, R. G. Preprint.
(8) Jähnig, F. *J. Chem. Phys.* **1979**, *70*, 3279.
(9) Khokhlov, A. R.; Semenov, A. N. *J. Phys. A: Math. Gen.* **1982**, *15*, 1361.
(10) ten Bosch, A.; Maissa, P.; Sixou, P. *Phys. Lett.* **1983**, *94A*, 299; *J. Chem. Phys.* **1983**, *79*, 3462.
(11) Rusakov, V. V.; Shliomis, M. I. *J. Phys. Lett.* **1986**, *46*, L-935.
(12) Warner, M.; Gunn, J. M. F.; Baumgärtner, A. *J. Phys. A: Math. Gen.* **1985**, *18*, 3007.
(13) Bladon, P.; Warner, M.; Cates, M. E. To be published in *Macromolecules*.
(14) d'Allest, J. F.; Wu, P. P.; Blumstein, A.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst. Lett.* **1986**, *3*, 103.