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Transesterification in Nematic Polymers

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ABSTRACT: Polydisperse melts of nematic polymer liquid crystals (PLC's) display a biphase region at the nematic–isotropic transition. We describe this phase separation for a melt of transesterifying chains. Transesterification, a process where chains exchange material at fixed overall chain number, results in an annealed rather than quenched polydispersity. The PLC is modeled as a wormlike chain with a Maier–Saupe nematic mean field. The phase diagram and length distribution are calculated. The biphasic gaps reported in experiments on transesterifying melts are discussed.

1. Introduction

Polymer liquid crystals (PLC's) are polymers with nematic units incorporated into the main chain or hung as pendants from the main chain. In this paper we shall describe only the case of main chain PLC's which exhibit prolate symmetry. However, there exist many types of side chain PLC's of the same symmetry, and our analysis will apply qualitatively to them as well and to oblate side chain systems. Polydisperse melts of nematic PLC's are of experimental interest.[1-9] At the nematic–isotropic (N–I) phase transition there is a phase gap, with a finite temperature range within which the system phase separates into two components, nematic and isotropic. In a purely monodisperse melt there should be no such phase gap (by the Gibbs phase rule). The phase gap has been interpreted in terms of a distribution of fixed (quenched) polydispersity by Semenov.[10] This is appropriate to immutable chains such as polyethers, but not to polyesters. Part of the interest in phase diagrams of polydisperse systems derives from the dependence of mechanical and rheological properties on any residual isotropic phase present.

In this paper we give a framework for interpreting experiments on polyesters in terms of a melt of transesterifying chains. Transesterification is the process where chains can swap ends (see Figure 1), with the total number of chains (and hence chain ends) remaining fixed. An initially monodisperse melt, when heated, will become polydisperse through this process. Deuteron-labeled chains in a protonated host lose their identity and a neutron scattering determination of chain size eventually becomes impossible.[7,8] This situation is intermediate between that of complete quenching[10] and full equilibrium (as arises, *e.g.*, for self-assembling micellar systems), in which not only the size distribution but also the total number of chains can vary.[11,12] We will see that in this case the total number of chains (or ends) per unit volume acts as a concentration-like variable, hence allowing a phase gap to appear: in effect one has a two-component system. (The same does not apply in the case of full equilibrium where one has instead only one conserved species, namely, monomer.)

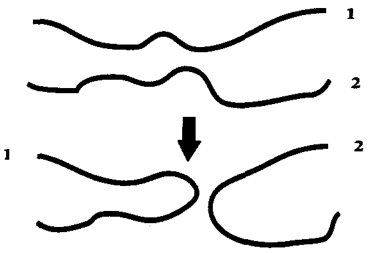

Figure 1. Transesterification: Chains 1 and 2 break and recombine, exchanging material in the process. This will cause an initially monodisperse melt to become polydisperse.

The neutron scattering papers[7,8] on nematic polyesters thus give the clearest evidence that transesterification can take place, at least at the elevated melt temperatures where scattering experiments were performed. Problems of interpretation can arise since these authors note that there are difficulties with the GPC measurements (M_w by this method and by light scattering vary widely) and hence perhaps with the M_w/M_n values quoted ($M_w/M_n = 2.4$), the fully annealed value being ≤2. Possibly this value is correct for polymers measured before annealing at higher temperatures where subsequent transesterification took place.

Transesterification has also been unequivocally seen in regular copolymers using NMR techniques.[5,6] Jin noted a randomization of regular copolymers in the melt phase, and Economy *et al.* extensively studied transesterification during polymerization, during annealing, and in melt phases of regular copolymers.

A lengthy and careful investigation of polydispersity effects on phase diagrams of polymer liquid crystals was carried out on the polyesters known as DDA9 and AZA9.[1-4] Great care was taken to fractionate and study samples below 160 °C whence it was assumed that no degradation or "reorganization" took place. GPC before and after experiments confimed that the molecular weight distribution did not change. Accordingly, we assume that this work is unrelated to our considerations of transesterification.

The phase study[1] included fractionation experiments separating the isotropic and nematic phases in the biphasic gap. Subsequent analysis showed that the longer chains were preferentially in the nematic phase. The onset of nematic behavior in a subsequent phase analysis of two separated samples showed that the formerly nematic sample had a much higher temperature stability for its nematic phase than did the formerly isotropic sample. This suggests a lower nematic free energy per monomer for longer chains than for shorter chains, an observation at the core of this problem.

The emphasis in this paper is modeling the system as simply as possible in order to understand the underlying physics. We use a wormlike chain description for the polymer with the nematic interaction included via a Maier–Saupe-like mean field; thus chain–chain interactions are replaced by a mean field. The entropy of the chains is estimated using a Flory–Huggins expression for the distribution of chains which are inscribed on a lattice. The wormlike chain model is the minimal model that will have a phase gap since the chain ends have a different degree of ordering and hence a different contribution to the free energy than the middle segments of the chain, as noted by Semenov.[10,13] In this model each chain has a free energy per segment length and an additional contribution to the free energy which can be interpreted as an "end" energy. Other models, *e.g.*, the freely jointed rod model, only have a free energy per segment length, as neighboring segments are uncorrelated. Hence there will be no incentive for chains of different lengths to alter their partitioning between different states of nematic order and the freely jointed rod model will not produce a biphasic region.

In section 2 we give a brief review of the wormlike chain theory of PLC's. In section 3 we calculate the free energy for the system and reduce the problem to one of a gas of chain ends on a lattice. The numerical results are presented in section 4, and in section 5 we conclude.

2. The Wormlike Chain Theory of Nematic Polymers

A worm chain in a nematic field has been reduced to a spheroidal wave equation by a number of authors.[14-17] Here we outline the essential points and refer the reader to ref 18 for a fuller description. A wormlike chain is represented as a continuous curve which pays a bending energy penalty per unit length with stiffness ϵ. Each infinitesimal length of the chain feels and contributes to a nematic mean field, Q, where Q is given by

$$Q = \langle P_2(\cos\theta(s))\rangle \tag{1}$$

where P_2 is the second Legendre polynomial, and $\cos\theta(s)$ is the angle that the tangent vector $\mathbf{u}$ of the chain makes at a point s along the chain with the director, chosen to be the z direction. The problem can be mapped onto a spheroidal diffusion equation

$$(\lambda_n + \nabla^2 + \Delta_Q{}^2 P_2(\cos\theta))\mathrm{Sp}_n = 0 \tag{2}$$

$\Delta_Q{}^2 = \beta\nu Q l_0$ is a coupling constant representing the strength of the nematic potential in the diffusion equation, where $\beta = 1/k_BT$, Q is the order parameter, ν is the nematic interaction energy, and $l_0 = 1/D = 2\beta\epsilon$ is the inverse angular diffusion constant, which characterizes the worm chain in the absence of nematic fields; λ_n is the eigenvalue of the diffusion equation; and ∇^2 is the angular part of the Laplacian. Note that eq 2 is not the standard form of the zero-order spheroidal wave equation,[19] as the potential is of the form $\Delta_Q{}^2P_2$ rather than the standard $\cos^2\theta$-like term. The relationship between coupling constant and eigenvalues used by Warner *et al.* in previous work is $\Lambda_0 = \lambda_0 - {}^2/_3\Delta^2$, where $\Delta^2 = -{}^2/_3\Delta_Q{}^2$. The Sp_n wave functions are normalized to one instead of the normal value and are the spheroid equivalent of the spherical functions $Y_l{}^m(\theta,\phi)$. The Green function for the wave equation (2) is

$$G(\mathbf{u},\mathbf{u}_0;L,0) = \sum_n \mathrm{Sp}_n(\mathbf{u})\,\mathrm{Sp}_n(\mathbf{u}_0)\exp(-\lambda_n L/l_0) \tag{3}$$

The propagator G can be used to evaluate the partition function and the conformations of the chain.[18] The partition function is

$$Z = \int \mathrm{d}\mathbf{u}\,\mathrm{d}\mathbf{u}_0\, G(\mathbf{u},\mathbf{u}_0;L,0) \tag{4}$$

If the chains are very long, L is large; then the partition function, Z, becomes dominated by the first term in the sum, and the term $-k_BT\ln Z$ in the free energy can be replaced by the lowest eigenvalue of the diffusion equation. The term containing the integral of the wave function is ignored in this limit. This "long-chain" limit is analogous to ground state dominance in a quantum mechanical system at long times. However, we are interested in cases where the chains in the system have a distribution of lengths, and consequently more terms in the partition function have to be retained than just the lowest eigenvalue. The size of the next term in the sum is governed by $\exp(-\lambda_2L/l_0)$. The unperturbed value of λ_2 is 6 (*i.e.*, the value when $\Delta_Q{}^2 = 0$), and λ_2 diverges from λ_0 with increasing Q—see ref 18. Therefore we neglect all higher terms except the first term in the partition function but retain the integral of the wave function. The free energy per chain can then be written as

$$\frac{F_{\mathrm{chain}}}{k_BT} = \lambda_0\frac{L}{l_0} - \ln\left[\int \mathrm{d}\mathbf{u}\,\mathrm{Sp}_0(\mathbf{u})\right]^2 + \frac{1}{2}\beta\nu Q^2 L \tag{5}$$

The extra term in the free energy, not deriving from $-k_BT\ln Z$, arises from the need to eliminate the double counting introduced by the mean field. The eigenvalue term λ_0 is the nematic energy per chain segment of an infinitely long chain and scales linearly with chain length. The log term can be thought of as the energy of a pair of chain ends as it is independent of the chain length and will henceforth be denoted by E_Q. It is a deviation from the long-chain nematic energy due to the extra freedom the ends enjoy. Expressed in terms of the coupling constant $\Delta_Q{}^2$ and introducing a reduced temperature $\tilde{T} = k_BT(\nu\epsilon)^{1/2}$, the free energy per chain is

$$\frac{F_{\mathrm{chain}}}{k_BT} = \frac{L}{l_0}\left[\lambda_0 + (\Delta_Q{}^2)^2\frac{\tilde{T}^2}{4}\right] - E_Q \tag{6}$$

A monodisperse melt of infinitely long chains, where the E_Q term can be ignored, has a nematic–isotropic phase transition temperature of $\tilde{T} = 0.38775$.[20] If we wish to express the free energy of a wormlike chain in terms of the number of monomers i that make up the chain, we must divide by Flory's $C_\infty = l_0/a$. C_∞ is the number of monomers in a persistence length and therefore

$$\frac{L}{l_0} = \frac{ai}{l_0} = \frac{i}{C_\infty} \tag{7}$$

To gain some insight as to how the addition of the energy E_Q affects the properties of the wormlike chain, we can develop a Landau theory and investigate the effect of the new term(s) introduced to the free energy. The E_Q term arises from the wormlike chain model as the square of the integral of the lowest eigenfunction. The eigenfunction is expanded in terms of the spherical harmonics, the $Y_l{}^m$'s, and contains only terms with even values of l, which are even functions. The only term to contribute to the integral is the constant term. Doing the integration multiplies the constant term by a factor which can be discarded when we take the log, as it just adds another constant to the free energy which is independent of Q.

The result of a perturbation analysis of the spherical diffusion equation gives the following (writing $\Delta_Q{}^2 = \eta$ to simplify notation):

$$\frac{F_{\mathrm{chain}}}{k_BT} = \frac{i}{C_\infty}\left[\frac{A}{2}\eta^2 + \frac{B}{3}\eta^3 + \frac{C}{4}\eta^4\right] + \frac{\alpha}{2}\eta^2 + \frac{\beta}{3}\eta^3 + \frac{\gamma}{4}\eta^4 \tag{8}$$

where the constants are

$$A = \left(\frac{\tilde{T}^2}{2} - \frac{1}{15}\right)$$

$$B = -1/310$$

$$C = 13/47250 \tag{9}$$
$$\alpha = 1/90$$
$$\beta = 1/630$$
$$\gamma = -269/2835000$$

We want to examine the effect of the new terms on the phase transition temperature and the jump of the order parameter at the transition point. The transition temperature is given by

$$\frac{\tilde{T}_c^{\,2}}{2} = \frac{2B^2}{9C}\left(1 + \left(\frac{\beta}{B} + \kappa\right)\frac{C_\infty}{i} + ...\right) + \frac{1}{15} - \alpha\frac{C_\infty}{i} \tag{10}$$

where $\kappa = \beta/B - \gamma/C \sim 10^{-2}$ is small. Terms smaller than κ have been dropped in the expansion. The extra two terms that modify the long-chain result (the terms containing C_∞/i) are both negative, as $\beta/B = -1/3$, and α is positive. This results in a lowering of the transition temperature to smaller values of $\tilde{T}$ with increasing values of the ratio C_∞/i; *i.e.*, shorter or stiffer chains have a lower transition temperature.

The jump in the order parameter at the transition point is given by

$$\eta_{\text{jump}} = -\frac{2B}{3C}\left[1 + \kappa\frac{C_\infty}{i}\left(1 + \frac{\gamma}{C}\frac{C_\infty}{i}\right)\right] \tag{11}$$

Therefore η_{jump} is essentially unaffected by the extra energy E_Q.

3. The Free Energy of a Distribution of Chains

We calculate the free energy of a distribution of chains using a Flory–Huggins lattice theory.[21] The entropy of noninteracting chains of length i monomer units is given by

$$-\frac{S}{k_B} = Vc_i \ln c_i \tag{12}$$

where $c_i = n_i/V$ is the number density of chains of species with length ai and where there are n_i such chains in a volume V; a is the size of one lattice site. We assume each monomer is isodiametric and occupies one lattice site. The free energy, F, per lattice site of a set of chains c_i is

$$\frac{F}{k_BT} = \sum_i a^3c_i[\log c_i + if_i] \tag{13}$$

where f_i is the nematic free energy per lattice site of species i. Dividing by a^3, F will henceforth be a free energy per unit volume and be in units of k_BT. The free energy is separable into an entropy term and an energy term because the chains do not interact directly with each other, only via the mean field.

The total order parameter Q appearing in the mean field is a monomer-concentration-weighted sum of the order parameters of the individual species Q_i

$$Q = \sum_i ic_iQ_i \tag{14}$$

The nematic free energy per lattice site of the ith species, f_i, is

$$f_i = \frac{1}{C_\infty}\left[\lambda_0 + \frac{\beta}{2}\nu QQ_il_0\right] - \frac{E_Q}{i} \tag{15}$$

The mean field term is now $\beta\nu QQ_il_0/2$, and using eq 14 we can remove the mean field term from the sum and replace it by the same mean field term as that occurring in (6). Inserting (15) into (13) the free energy is

$$F = \sum_i c_i\left[\ln c_i + \frac{i}{C_\infty}\lambda_0 - E_Q\right] + \frac{\tilde{T}^2}{4C_\infty}(\Delta_Q^{\,2})^2 \tag{16}$$

The equilibrium length distribution c_i should minimize the free energy subject to the two constraints that the volume of material is constant and the number of chain ends is fixed. These two constraints are

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

The first condition give C_e, the concentration of chains (so $C_e = {}^1/_2C_{\text{ends}}$, where C_{ends} is the concentration of ends). The second condition specifies that the melt has one monomer per lattice site. To express these two constraints via Lagrange multipliers, μ and λ, we add $\mu\sum_ic_i + \lambda\sum_iic_i$ to the free energy (15). Here μ and λ are in effect chemical potentials which are chosen to give the correct density of chain ends and monomers, respectively. Minimizing the free energy with respect to c_i leads to

$$\frac{\partial F}{\partial c_i} = 0 = 1 + \ln c_i + \frac{i\lambda_0}{C_\infty} - E_Q + \mu + i\lambda \tag{18}$$

resulting in an exponential distribution for c_i

$$c_i - A\mathrm{e}^{-i(\lambda_0/C_\infty + \lambda)} \tag{19}$$

The prefactor A hides all the i-independent terms. Given that c_i is of the form $c_i = Ax^i$, putting this in (17) gives conditions on A and x (the latter fixing λ, the former μ) on summing the geometric series:

$$x = 1 - C_e \tag{20}$$
$$A = \frac{C_e^{\,2}}{1 - C_e}$$

The length distribution is therefore obtained as

$$c_i = C_e^{\,2}(1 - C_e)^{i-1} \tag{21}$$

Thus the distribution depends on whether one is in the isotropic or nematic phase only through the simple variable C_e.

The quantity $1/C_e$ is equal to the average chain length L in monomer units. Given the simple form $c_i = Ax^i$ for the distribution, any moment can be calculated, including the weight average

$$L_w = \sum_i ic_ii/\sum_i ic_i \tag{22}$$

The denominator has been constrained to be 1 and summing the numerator yields

$$L_w = \frac{2}{C_e} - 1 \tag{23}$$

Therefore the ratio $M_w/M_n \equiv L_w/L$ can be calculated and is equal to

$$M_w/M_n = 2 - C_e \tag{24}$$

The ratio M_w/M_n in a system which is transesterifying is therefore always less than 2. The free energy is now

$$F = 2C_e \ln C_e + (1 - C_e)\ln(1 - C_e) + \tilde{f} \tag{25}$$

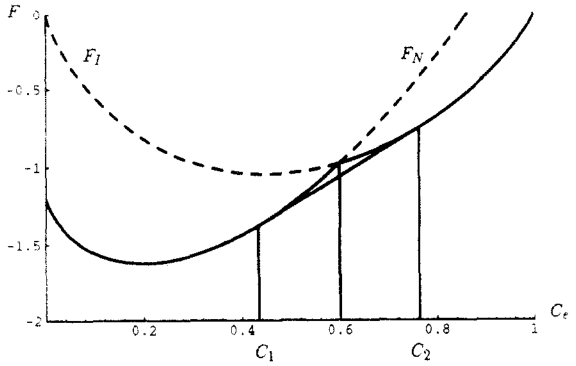

Figure 2. Schematic plot of the free energy showing the isotropic (F_I) and nematic (F_N) branches. The metastable phases are indicated by dashed lines. In the region $C_1 \rightarrow C_2$ the system will phase separate into two phases with chain concentrations C_1 and C_2, which have a combined free energy lower than, for instance, the free energy indicated at $C_e = 0.6$. The common tangent is shown which embodies the phase coexistence conditions.

where $\tilde{f}$, using the conditions (17) in (16), obeys

$$\tilde{f} = \frac{1}{C_\infty}\left(\lambda_0 + \frac{\tilde{T}^2}{4}(\Delta_Q^{\,2})^2\right) - C_e E_Q \tag{26}$$

The free energy is similar to the free energy in the Flory–Huggins approximation of a gas of ends with an interaction energy $\tilde{f}$, which depends on the nematic order Q. The free energy F is a function of Q and has to be minimized with respect to Q or, equivalently, with respect to Δ_Q^2. This leads to the following self-consistency condition for Δ_Q^2.

$$\Delta_Q^{\,2} = \frac{2}{\tilde{T}^2}\left[C_e C_\infty \frac{\partial E_Q}{\partial \Delta_Q^{\,2}} - \frac{\partial \lambda_0}{\partial \Delta_Q^{\,2}}\right] \tag{27}$$

At a given C_e, C_∞, and $\tilde{T}$ this self-consistency condition has to be solved to obtain the equilibrium value of Δ_Q^2 and hence Q. Two solutions exist for Q, one with $Q = 0$, and one with $Q \neq 0$. The two branches of the free energy with $Q = 0$, $Q \neq 0$ will be referred to as F_I and F_N, respectively. Figure 2 schematically shows the free energy against chain end volume fraction at a given temperature and particular C_∞. If $C_e > C_2$, F_I has a lower free energy than F_N and the system is therefore isotropic. If $C_e < C_1$, the system will be in the nematic phase. If C_e lies between C_1 and C_2, the free energy at C_e is higher than the combination of two phases with $C_e = C_1$ and $C_e = C_2$. The system therefore phase separates into two phases henceforth denoted by C_1 and C_2. The conditions for the two phases to coexist, the common tangency conditions, are

$$\left.\frac{\partial F_N}{\partial C_e}\right|_{C_e=C_1} = \left.\frac{\partial F_I}{\partial C_e}\right|_{C_e=C_2} \tag{28}$$

$$F_N|_{C_e=C_1} - C_1\left.\frac{\partial F_N}{\partial C_e}\right|_{C_e=C_1} = F_I|_{C_e=C_2} - C_2\left.\frac{\partial F_I}{\partial C_e}\right|_{C_e=C_2}$$

The criteria we have discussed for phase coexistence are similar to those for a two-component system, and indeed we can think of the chain density C_e as an effective concentration variable. The system is then similar to a lyotropic nematogen in which the first-order isotropic–nematic transition is invariably accompanied by a miscibility gap. As noted earlier, if the melt of chains were in full thermodynamic equilibrium with respect to the total chain number (as well as the chain size distribution), such a miscibility gap would be impossible by the Gibbs phase rule.

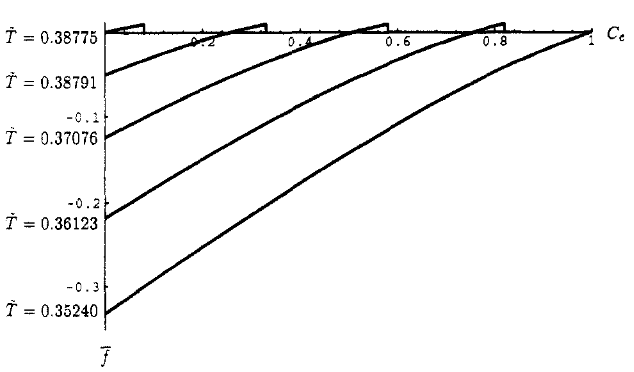

Figure 3. $\tilde{f}$ vs C_e is shown for $C_\infty = 1$ at the temperature indicated. $\tilde{f}$ is the effective interaction energy as a function of C_e. When $\tilde{T} = 0.35240$, $\tilde{f} < 0$ for the entire range of C_e, setting the lower bound on biphase behavior. The upper bound is set by $\tilde{T} = 0.38775$, where $\tilde{f}$ is always positive or equal to zero.

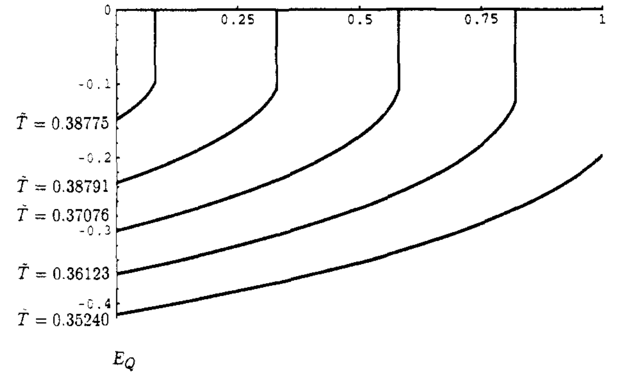

Figure 4. E_Q vs C_e is shown for $C_\infty = 1$ at the indicated temperatures.

4. Results

To see how the concavity in the free energy arises we plot $\tilde{f}$ at the equilibrium value of Q vs C_e for different values of the reduced temperature, with $C_\infty = 1$ as shown in Figure 3. In the region of C_e where $\tilde{f} < 0$, then $F_N < F_I$. For regions where $\tilde{f} > 0$, then $F_N > F_I$. For $T < 0.35240$ $\tilde{f}$ is negative for all values of C_e, and this sets the lower bound on the biphasic region, since if F_N is always less than F_I, there is no way in which a common tangent can be constructed. The upper bound is given by $T = 0.38775$, above which $\tilde{f}$ is always positive; that is, F_N is always greater than F_I and likewise no common tangent is possible. The approximately linear variation of $\tilde{f}$ with C_e allows an analysis of the ends of the phase diagram to be performed, which is presented in the Appendix.

The energy E_Q and the order parameter Q are shown in Figures 4 and 5. One can see that $E_Q \propto -Q$, but E_Q is not proportional to C_e. Since $\tilde{f}$ crosses the zero axis with a finite gradient, the meeting of the isotropic and nematic branches of the free energy occurs with a discontinuity in slope. Considering the common tangent construction and this discontinuity in slope, it is clear that coexsisting phases linked by this common tangent can never merge continuously into each other as a parameter (*e.g.*, temperature) is varied. This means that on the phase diagrams discussed below there can be no critical point.

Solving (28) for the specified $\tilde{T}$ range results in the phase diagram shown in Figure 6. Figure 7 shows the phase diagram in a more conventional representation on the $(L,\tilde{T})$ plane where the chain length is $L = 1/C_e$. Figure 8 shows the order parameter of a phase with $C_e = 0.6$ and Figure 9 the corresponding volume fraction of the nematic phase obtained by using the lever rule. The dashed line in Figure 8 is the order parameter of a monodisperse melt of chains

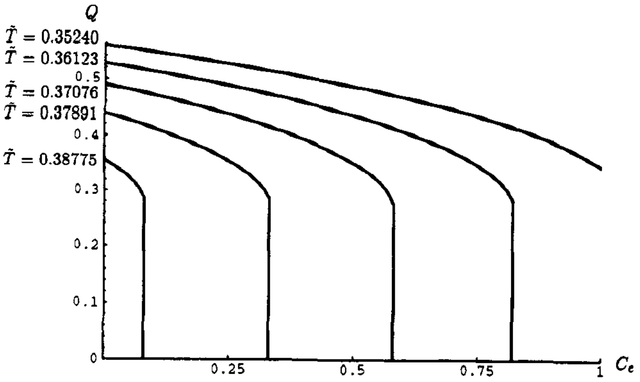

Figure 5. Q vs C_e is shown for $C_\infty = 1$ at the indicated temperatures. Notice how $Q \propto -E_Q$. The end energy sets the effective interaction energy, but is not itself proportional to C_e; it is highly nonlinear. The end energy and the other nematic energy terms have to be minimized together to form $\bar{f}$.

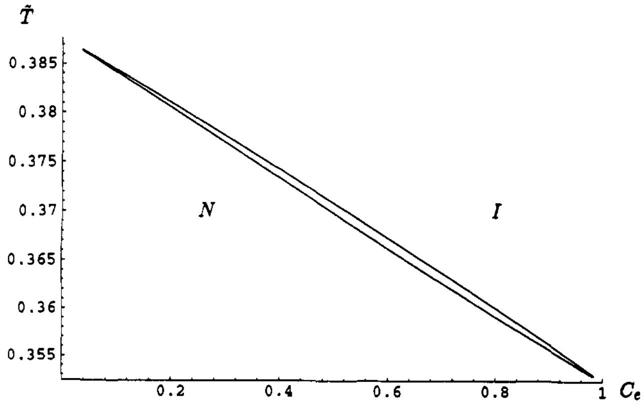

Figure 6. Phase diagram for $C_\infty = 1$.

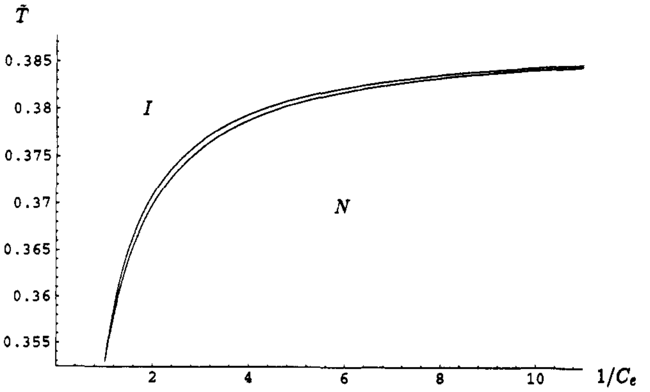

Figure 7. Phase diagram for $C_\infty = 1$ is shown plotted vs $1/C_e$, the number-average chain length.

with the same C_e. Before the monodisperse N–I phase transition temperature the system phase separates. The order parameter Q after phase separation shows a slight increase with increasing temperature. Instead of becoming less ordered with increasing temperature, the N phase throws out shorter chains into the I phase to reduce its free energy until the whole system becomes isotropic at $\tilde{T} \simeq 0.3674$.

Comparison with Experiments. In comparing our results to experiments we must scale our reduced temperature $\tilde{T}$ to that of the experiments. Matching the transition temperature of the model to the experimental transition temperature determines the value of $(\nu\epsilon)^{1/2}/k_B$. The other parameter that must be assigned a value is C_∞.

C_∞ arises because of the need to express the free energy per chain, given in persistence lengths in the $\lambda_0 L/l_0$ term of (6) and given in terms of the chain length $(^1/_2)\beta\nu Q^2 L$, as an average energy per lattice site. The effect of altering C_∞ from unity is to alter the weight attached to the end energy of the chains, as can be seen from (27). Increasing C_∞ therefore makes the gradient of $\bar{f}$ vs C_e steeper and widens the range of the biphasic region and the phase gap. Figure 10 shows the phase diagram with C_∞ set to 5. Also on the figure for comparison is the phase diagram when $C_\infty = 1$. The widening of the phase gap and the lowering of the transition temperature are very evident. Precisely what value of C_∞ should be taken is not entirely clear. The ratio $C_\infty = l_0/d$, where d is the monomer length, is available from neutron scattering determinations on the chain size in the isotropic melt. But in addition we are mapping a

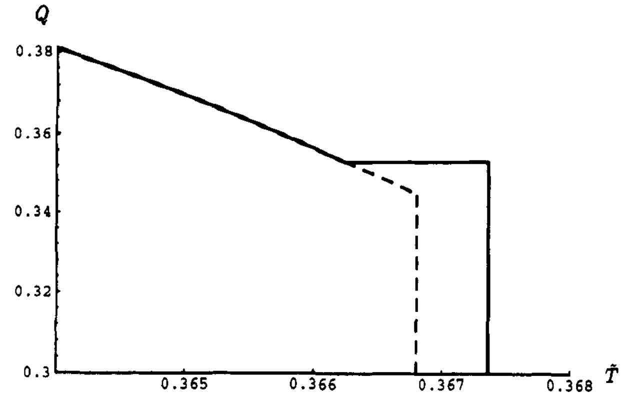

Figure 8. Order parameter Q vs $\tilde{T}$ for $C_\infty = 1$ at the point in the phase diagram where $C_e = 0.6$. The dashed line shows the order parameter of a monodisperse melt with $C_e = 0.6$. Before the monodisperse melt phase transition temperature the system phase separates. Increasing $\tilde{T}$ causes an almost imperceptible rise in Q as the system lowers its free energy by throwing out short chains into the isotropic phase. At $\tilde{T} = 0.3674$ the N phase becomes isotropic with a first-order transition.

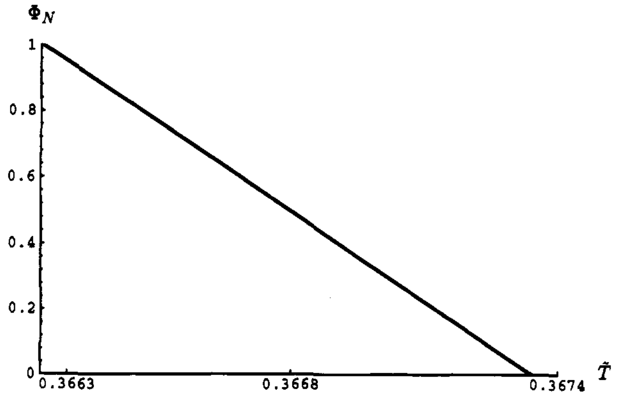

Figure 9. Volume fraction of nematic phase Φ_N vs $\tilde{T}$ is shown for $C_\infty = 1$ at the point in the phase diagram where $C_e = 0.6$. The decrease in Φ_N with $\tilde{T}$ is very nearly linear.

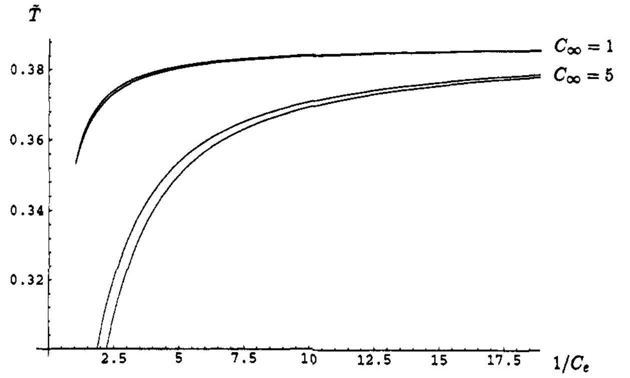

Figure 10. Phase diagram for two different values of C_∞ is shown vs $1/C_e = L$. Increasing C_∞, the persistence length, widens the phase gap and increases the range of temperature over which the system is biphasic.

problem with anisodiametric monomers onto an isodiametric lattice. In comparing our predictions to experiment it is perhaps safer to take C_∞ as a phenomenological parameter. It is obviously important to decide whether our model can describe the observed behavior without invoking unreasonable C_∞ values.

The temperature T in the wormlike chain model is given by $T = \tilde{T}(\nu\epsilon)^{1/2}/k_B$ where $\tilde{T}$ is the reduced temperature and is of the order unity (~0.388) at the N–I transition. Assuming that both ν and ϵ are T-independent allows us to establish a scale factor between $\tilde{T}$ and T_{exp}, the experimental transition temperature for long enough chains. In practice, for data on a set of samples of various chain lengths L, this scale factor can be found by fitting the overall shape of the phase boundary (*e.g.*, defined as the midline of the two-phase region).

In the neutron scattering experiments of Abis *et al.*[8] where transesterification was confirmed to have been taking place, the samples were biphasic from $T = 225$ to $T = 255$ °C. The polymers studied were copolyesters known as DMB which consists of a rigid unit joined by flexible spacers of length either 8 or 10 units. There was a 50/50 ratio between the two flexible spacers. In the two samples where the biphasic gap was reported, denoted by D2 and D8, the molecular weights were $M_w = 8600$ and 14800, respectively. The ratio M_w/M_n was not measured for the deuterated polymers used in the neutron scattering experiments, but we shall assume that it is the same as that measured in the nondeuterated chains, that is 2.4. The ratio M_w/M_n should be less than 2 for transesterifying chains—see below. This gives an average chain length of 8 and 13 units for D2 and D8, respectively. Scaling the calculated phase gaps and fitting C_∞ give values for C_∞ of 17 and 30 for D2 and D8, respectively. Although C_∞ should not be interpreted strictly as a persistence length, as discussed above, these values of C_∞ seem unreasonably large, particularly given the short chains used in the experiments.

The fact that the neutron signal is still obtained is evidence that transesterification is not yet complete. This is in concordance with $M_w/M_n = 2.4$. Greater than expected polydispersity will give wider phase gaps.[10] The system is effectively a random copolyester with different length (8 or 10 units) flexible spacers. This is then a multicomponent system. The width of the biphasic region is no longer a $1/N$ effect of chain ends but an $O(1)$ effect stemming from the wide range of compositional fluctuations possible. Obviously, it would be interesting to have detailed experiments on systems with only one type of spacer.

In the work of d'Allest *et al.* the authors believe their chains are immutable. Evidently the temperatures are too low and the times spent in the melt too short to allow transesterification to take place.

A recent work is that of Li *et al.*[9] These authors carefully studied the kinetics of transesterification in the isotropic phase of a mesomorphic main chain PLC by neutron scattering. They concluded that long times are required for transesterification to take place (several hours), in agreement with studies quoted above. Their conclusions about kinetics in the nematic phase were not as firm. Li *et al.* did not study phase gaps.

5. Conclusions

We have shown that in transesterifying main chain polymer liquid crystals the chain length distribution remains exponential, just as it is in the isotropic phase. However, since the free energy per monomer on a chain differs according to whether the chain is long or short, there is a selective partitioning of long chains to a nematic phase and short chains to the coexisting isotropic phase. A biphasic region arises which can be described in terms of the number density of chains in the melt, which plays the role of a conserved concentration variable. The form of the phase diagram (Figure 6) and the connection $L = 1/C_e$ suggest a fractionation scheme to separate short from long chains. From a nematic phase with a given C_e, heating drives one into the biphasic gap and the nematic phase will select the longer chains. Separation of this phase and repetition of the process will see the mean chain length continue to grow. It would be interesting to perform fractionation to test this description. A systematic study, parallel to that of d'Allest *et al.*,[1] would be most revealing. Experiments already performed on nematic polyesters have established the time scale for transesterification by measuring the t-dependence of the disappearance of the neutron scattering signal from a blend of deuterated and protonated polymers.[7,8] These authors have also demonstrated that light scattering experiments to determine M_w are perfectly feasible. While there is no doubt that transesterification takes place, the effect on the phase diagram is unclear, as insufficient evidence that is free from polydispersity effects is available.

The analysis of Semenov,[10] which we received as a preprint on completeion of this work, attacks the related problem with quenched polydispersity. His method is of great generality. He too recognizes that there is an end engery per chain ($= {}^1/_2 E_Q$), in addition to an energy per monomer, which causes shorter chains to fractionate from longer chains. This energy he leaves as an arbitrary, model-dependent quantity. He obtains general analytic results for the width of the phase gap in temrs of this energy and the overall distribution of chain lengths but does not account for the effects of transesterification as addressed in this paper.

It remains a future problem to describe the *dynamics* of readjustment of the chain size distribution in response to changes in the biphasic equilibrium. It is not parallel to the dynamics described in "living polymers" T-jumps[12] since the distribution is T-independent. Rather it is the rate of repartitioning of chain ends between coexisting bulk phases that must be described, an effect that will depend on the sample morphology of the microphases that emerge. These remarks are equally applicable to non-transesterifying systems too, for instance in ref 1.

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Appendix. Analytic Remarks about the Form of the Phase Diagram

The quantity $\bar{f}$ in (26) has an explicit dependence on C_e (the $-C_eE_Q$ term) and presumably a buried implicit dependence through the value of Q appearing in λ_0, Δ_Q^2, and E_Q, since at equilibrium Q is a self-consistently-determined value, its equation (27) involving C_e. However, the linearity of Figure 3 ($\bar{f}$ vs C_e) suggests the implicit dependence of $\bar{f}$ on C_e is very weak. We can thus write

$$\bar{f}/k_BT = DC_e - (D - \delta) \qquad (29)$$

Figure 11 shows the construction of $\bar{f}$. We want to analyze both ends of the phase diagram, where $C_e \rightarrow 0$ and $C_e \rightarrow 1$. For the limit $C_e \rightarrow 0$ the quantity $D - \delta$ is small, positive,

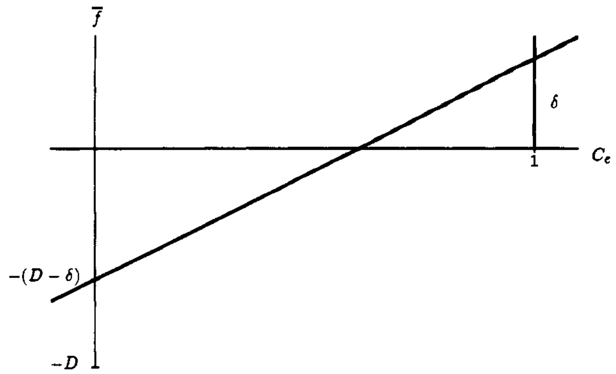

Figure 11. Construction of $\bar{f}$ vs C_e.

and tends to zero. For the limit $C_e \rightarrow 1$, the quantity δ is small and tends to zero. Thus we can analyze both ends of the phase diagram analytically if we assume that $\bar{f}$ has the form of (29).

We rewrite the two common tangent conditions as

$$\frac{C_1^{\,2}}{C_2^{\,2}}e^{D} = \frac{1-C_1}{1-C_2} \tag{30}$$

$$F(C_1) - F(C_2) = (C_1 - C_2)\frac{\partial F}{\partial C_2}$$

To analyze the limit $C_e \rightarrow 1$ we make the substitutions $C_1 = 1 - \epsilon_1$ and $C_2 = 1 - \epsilon_2$ for the nematic and isotropic concentrations, respectively. The first common tangency condition is easily solved to first order and we obtain

$$C_1 \sim C_2 e^{-D/2} \tag{31}$$

$$\epsilon_1 \sim \epsilon_2 e^{D}$$

Substituting into the other condition one obtains at first order for the C's

$$C_1 \sim \frac{(D-\delta)e^{-D/2}}{2(1-e^{D/2})} \tag{32}$$

$$C_2 \sim \frac{D-\delta}{2(1-e^{D/2})}$$

and for the ϵ's

$$\epsilon_1 \sim \frac{\delta e^{D}}{e^{D}-1} \tag{33}$$

$$\epsilon_2 \sim \frac{\delta}{e^{D}-1}$$

As $T \rightarrow T^{(\min)}{}_{\mathrm{NI}}$, the lower temperature on Figure 6, $\delta \rightarrow 0$ tends to zero. As $T \rightarrow T^{(\max)}{}_{\mathrm{NI}}$, the highest temperature on Figure 6, $D - \delta \rightarrow 0$. Therefore close to $C_e = 1$ we can set $\delta = \delta_0(T - T^{(\min)}{}_{\mathrm{NI}})$, and close to $C_e = 0$ we can set $D - \delta = \omega_0(T^{(\max)}{}_{\mathrm{NI}} - T)$ with a constant slope D, with δ_0, ω_0, and D chosen to linearize the T and C_e behavior to the correct values for each end of the phase diagram. Putting this T-dependence into (32) and (33), one obtains for the limiting slopes of the phase diagram, for small C_e

$$\left.\frac{dT}{dC_e}\right|_{\text{nematic}} = \frac{2(e^{-D/2}-1)}{\omega_0 e^{-D/2}}$$

$$\left.\frac{dT}{dC_e}\right|_{\text{isotropic}} = \frac{2(e^{-D/2}-1)}{\omega_0} \tag{34}$$

and for large C_e

$$\left.\frac{dT}{dC_e}\right|_{\text{nematic}} = \frac{1-e^{D}}{e^{D}\delta_0}$$

$$\left.\frac{dT}{dC_e}\right|_{\text{isotropic}} = \frac{1-e^{D}}{\delta_0} \tag{35}$$

The slopes of the phase diagram are all negative. At the small C_e end, the slope of the nematic line is greater than that of the isotropic phase line. At the $C_e \sim 1$ end of the phase diagram, the nematic phase line has a smaller gradient than the isotropic phase line, as expected. The ratios of slopes of the nematic to isotropic phase lines at the small and large C_e ends of the phase diagram are $r_1 = e^{D/2}$ and $r^2 = e^{-D}$, respectively. Moreover, $r_1 = (1/r_2)^2$, as a result independent of any parameters or molecular characteristics within the limitations of (29).

The quantity D can be obtained from the theory. It is defined simply as

$$D = \left.\frac{\partial \bar{f}}{\partial C_1}\right|_{Q=Q_{\min}} \tag{36}$$

The order parameter Q is implicitly a function of C_1 through the required self-consistency condition for Q. Recognizing this, we can write

$$\frac{\partial \bar{f}}{\partial C_1} = -E_Q + \frac{\partial Q}{\partial C_1}\frac{\partial \bar{f}}{\partial Q} \tag{37}$$

The second term above must be zero from the requirement that Q must minimize the free energy (the self-consistency condition) and hence, $\bar{f}$, giving simply that $D = -E_Q$.

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