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Monodisperse Polymer Liquid Crystals near the Anisotropic–Isotropic Transition

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ABSTRACT: Polymer liquid crystal (PLC) macromolecules consisting of LC and flexible sequences are considered, particulary at the phase transition LC–i from an anisotropic to the isotropic phase. The Flory lattice model is used for formulation of the partition function; the orientation distribution function for LC interactions introduced by Flory and Ronca is included. While Flory and collaborators have improved the original Flory theory by taking into account the Maier and Saupe molecular mean field theory of liquid crystallinity, we now use the Landau approach for calculating the Helmholtz function of the system as a function of the orientation parameter s. This leads to formulas for parameters of the model in the vicinity of the LC–i transition. The critical values at the transition of the strength of orienting interactions s, the system temperature, and the anisotropy of LC sequences are calculated and discussed. The treatment is limited to monodisperse systems.

1. Introduction and Scope

Our approach to polymer liquid crystal (PLC) systems is based on the Flory lattice theory described in his fundamental papers[1,2] in 1956. Subsequently, the theory was applied by Flory and collaborators[2–14] to provide statistical descriptions of a number of specific cases, such as rods in solution in which interparticle forces, apart from repulsions on contact, are neglected; systems with orienting interactions between rods; polydisperse rods plus quasi-spherical molecules of the solvent; two types of rods with different axial ratios plus solvent; and rods connected by flexible joints plus solvent.

In this paper we consider systems of PLC macromolecules consisting of LC and flexible segments with varying concentrations of the LC segments. In the absence of internal interactions one can use the treatment of such macromolecules by Matheson and Flory.[11] To take into account orienting interactions, one can use the distribution function for orientations derived by Flory and Ronca.[4] In an earlier paper[15] the theory of Matheson and Flory was adopted with a modification accounting for the presence of the orientational interactions according to Flory and Ronca. The objectives of the present paper are 2-fold. The first is the computation of pertinent parameters in the vicinity of the liquid-crystal-to-isotropic (LC–i) phase transition using the Matheson–Flory theory[11] amplified in ref 15. The second aim is to find a criterion for the stabilities of the phases involved. The criterion will be obtained by using the Landau method[16] of relating the Helmholtz function of the system to an orientation parameter. As a result, we shall be able to obtain the phase diagrams of PCL copolymer systems as a function of the concentration θ of the LC sequences in the chains.

The LC phases under consideration are not limited to nematics. This is consistent with the original work of Flory; the generality of the approach was noted by Matheson.[14] What we briefly call LC phases are the same as the orientationaly ordered phases of Matheson.

2. Theoretical Framework

The lattice model requires the assumption that a segment constituting the unit portion of the chain has a length equal to its diameter and is of the same size as a cell in a cubic lattice. One also assumes that only one segment can be accommodated by a cell of the lattice. The second assumption takes care of the "excluded volume" effect. There are no vacancies in the lattice, so that the number of lattice sites N is the same as the total number of segments in the system. The approach can be extended to systems containing liquids (solvents) by taking also each liquid molecule as isometric with the lattice cell, a device used often by Flory and collaborators in papers already quoted, by Guggenheim,[17] and also in ref 18. In order to conform to the requirements of the lattice consisting of a cubic array of sites, each macromolecule is represented by a number of sequences of segments, each sequence parallel to the preferred axis. The preferred axis of a given sequence is taken along one of the principal axes of the lattice. This device has been also introduced by Flory[1,2] and is discussed in some detail in ref 15.

Our system consists of N_p copolymer chains, each of them made up of flexible (coiled) and liquid-crystalline relatively rigid (rodlike) sequences in alternating order. Each copolymer is supposed to consist of r unit segments, of which r_c belong to flexible sequences and r_h to rigid sequences, hence $r = r_c + r_h$. Thus, r is equal to the degree of polymerization. The parameter θ as defined above can then be calculated as $\theta = r_h/r$. The chains may differ from each other in three respects: the number of sequences (n of each type) in a copolymer chain; their length distribution (as characterized for instance by the average length η_h of a rodlike sequence); the relative position of a sequence in the copolymer chain. The parameters are related by

$$r = r_c + r_h = n(\eta_c + \eta_h) \qquad (1)$$

where η_c is the average length of a flexible sequence in each chain. For the purpose of this paper we assume the systems are monodisperse. The assumption that there are no vacancies in the cubic lattice leads to the relation $N = rN_p$.

The partition function for the system under consideration can be written as

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$$Z = Z_{\mathrm{comb}} Z_{\mathrm{orient}} \tag{2}$$

where Z_{comb} is the combinatorial or "steric" contribution and Z_{orient} is the factor describing the various orientations of the rigid sequences with respect to anisotropic repulsive interactions on contact as well as the influence on orientations of potential orienting interactions. The Helmholtz function of the systems is defined by the standard formula

$$A/kT = -\ln Z = -\ln Z_{\mathrm{comb}} - \ln Z_{\mathrm{orient}} \tag{3}$$

$\ln Z_{\mathrm{comb}}$ represents primarily the entropic contribution to the Helmholtz function, taking into account the number of ways the lattice sites can be occupied: $\ln Z_{\mathrm{orient}}$ is of entropic as well as energetic origin, the latter stemming from orienting interactions. The reduced Helmholtz function per molecule $\tilde{A}$ follows from (3) as

$$\tilde{A}/kT = -(\ln Z_{\mathrm{comb}} + \ln Z_{\mathrm{orient}})/N_{\mathrm{p}} \tag{4}$$

and, by using the Stirling approximation, takes the form[15]

$$\tilde{A}/kT = \ln r + r\left\{\left(1 - \frac{1}{r}\right) - (1 - Q)\ln(1 - Q) - Q - (1 - Q)\ln q_{\mathrm{c}}\right\} - \frac{n\eta}{N_{\mathrm{p}}}\{\ln f_1 + \gamma\,\langle\sin\psi\rangle + (\theta/\tilde{T})s(1 - s/2)\} \tag{5}$$

Here q_{c} is the internal partition function for each flexible sequence; the analogous partition function for the rodlike sequence is set equal to unity. The parameter $\bar{\eta}$ denotes a mean value of the length of rigid sequences in the system. The orientation parameter s is the average of the second Legendre polynomial $\langle P_2\rangle$ corresponding to the distribution function for the system and is equal to zero for a completely random (isotropic) phase and equal to unity when all rodlike sequences are exactly parallel to each other. The quantity Q is defined as

$$Q = \theta(1 - \bar{y}/\bar{\eta}) \tag{6}$$

Here $\bar{y}$ is the average of the Flory disorientation parameter; individual $\bar{y}$ is a measure of the deviation of a given sequence from the LC director axis. For a graphical representation see for instance ref 15. It must be noted that the mean values $\bar{\eta}$ and $\bar{y}$ are defined each by normalized sums of finite numbers of terms. Strictly speaking, the quantities $\bar{\eta}$ and $\bar{y}$ should constitute averages of infinite sums. For the monodisperse system considered here, the quantities $\bar{\eta}$ and $\bar{y}$ are unequivocally defined by finite sums of terms with the same value. For polydisperse systems the problem is not entirely trivial and will be considered in a later paper in this series.

For the equilibrium distribution of orientations the quantity γ in eq 5 has the form[15]

$$\gamma = -\frac{4\bar{\eta}}{\pi}\ln(1 - Q) \tag{7}$$

The average $\langle\sin\psi\rangle$ as well as the average s are calculated with the distribution function of orientations proportional to

$$\exp\left(-\gamma\sin\psi - \frac{3}{2}\theta s\tilde{T}^{-1}\sin^2\psi\right) \tag{8}$$

and normalized to unity. The first term in the parentheses corresponds to the interparticle repulsive forces on contact; the second term is related to the attractive orienting interactions. The reduced temperature $\tilde{T}$ in eqs 5 and 8 is defined as

$$\tilde{T} = T/\bar{\eta}T^{*} \tag{9}$$

where T^{*} is a characteristic temperature which serves as a measure of the strength (energy) of interactions between rigid sequences. f_1 in eq 5 denotes the normalization constant of the distribution function of orientations and is given by

$$f_j = \int_0^{\pi/2}\sin^j\psi\,\exp\left(-\gamma\sin\psi - \frac{3}{2}\theta s\tilde{T}^{-1}\sin^2\psi\right)\mathrm{d}\psi \tag{10}$$

with $j = 1$. Equation 10 also serves for $j > 1$, so that $f_2 = \langle\sin\psi\rangle$; $f_3 = \langle\sin^2\psi\rangle$, etc.

On the basis of the above definitions and equations we can now formulate conditions for the LC–i phase equilibrium of the system in question.

3. Conditions for the LC–i Phase Equilibrium

The Helmholtz function of the system depends on several variables, namely $A = A(\bar{y},\bar{\eta},s,\tilde{T};\theta)$. We can specify the concentration θ of the LC sequences and write

$$A = n_1\,\tilde{A}^{\mathrm{aniso}} + n_2\,\tilde{A}^{\mathrm{iso}} \tag{11}$$

The numbers of particles n_1 and n_2 pertain respectively to the anisotropic and isotropic phases. We have to apply the general phase equilibrium condition, namely that the variation

$$\delta A = 0 \tag{12}$$

with respect to all model parameters. As shown by Matheson and Flory,[11] the function A satisfies that equilibrium condition with respect to $\bar{y}$ and $\bar{\eta}$. The equation $\tilde{A}^{\mathrm{aniso}} = \tilde{A}^{\mathrm{iso}}$ describes an equilibrium between an isotropic and an anisotropic phase with respect to the numbers of particles n_1 and n_2. For the isotropic phase we have $s = 0$, $\bar{y} = \bar{\eta}$, so that $\theta = 0$ (as it should be), and $f_1 = 1$ (see ref 15). Expressing $\tilde{A}^{\mathrm{aniso}}$ and $\tilde{A}^{\mathrm{iso}}$ in terms of eq 5, we obtain the following equation valid at the LC–i phase equilibrium:

$$\bar{\eta}(1 - \theta)\ln(1 - Q) + \bar{\eta}Q + \theta[\ln f_1 + \theta s\tilde{T}^{-1}(1 - s/2)] = 0 \tag{13}$$

4. Conditions around the LC–i Equilibrium

Equation 13 does not include explicit information on the system stability with respect to ordering, i.e. with respect to s. Therefore, the criterion for the system stability with respect to s is needed, compatible of course with eq 12. We shall now derive such a criterion following a method due to Landau.[16] The choice is dictated by the simplicity of the method which gives simple conditions for the system in isotropic and/or anisotropic phases.

We proceed as follows. In the absence of an external orienting field, the Helmholtz function may be expanded as a power series of the order parameter s, leading to the following expression:

$$A = A_0 + \frac{1}{2}A_2 s^2 + \frac{1}{3}A_3 s^3 + O(s^4) \tag{14}$$

All these terms are invariant to any rotation of the Cartesian coordinates (x, y, z), as they should be. The coefficient A_2 is positive. We note that there is no term linear in s; this ensures that the minimum state corresponds to $s = 0$, that is, to the isotropic phase.

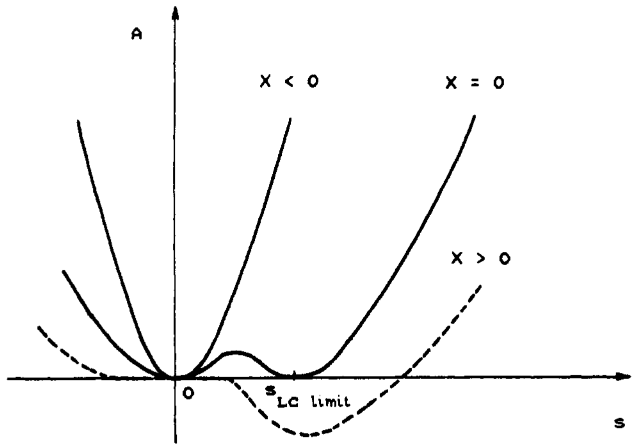

Figure 1. Free energy A as a functions of the order parameter s for various ranges of the parameter X as defined by eq 15. Explanation in text.

It is important to realize that in an anisotropic phase there is a nonvanishing term of the order s^3; the reason for this is the absence of a symmetry relation between the states s and $-s$.

For A_2 tending to zero and for non-zero finite A_3 the isotropic phase is completely unstable with respect to any anisotropic ordering. When the coefficient A_3 tends to zero, we observe the anisotropic–isotropic phase transition. In this case the isotropic and anisotropic phases coexist. A qualitative explanation of this situation is given in Figure 1. The three curves pertain to different values of the parameter X defined as

$$X = \theta/\tilde{T} - (\theta/\tilde{T})_{\text{LC limit}} \tag{15}$$

The subscript limit pertains to the lowest $\theta/\tilde{T}$ ratio at which a LC-rich, that is, orientationally ordered, phase can appear.

In an analogy to the Maier and Saupe theory[24,25] of liquid crystallinity, the ratio $\theta/\tilde{T}$ was introduced by Flory and Ronca[4] as a measure of the intensity of orienting interactions between a hard sequence and the molecular orienting field. The physical interpretation of $\theta/\tilde{T}$ will be more clear if the main steps of the Maier and Saupe theory are recalled. In the first step they consider the energy of interactions between two induced dipoles i and j with cylindrical symmetry. Truncating the expression for energy on terms of the order of r_{ij}^{-6} they obtain

$$\epsilon_{ij} = -Cr_{ij}^{-6}(\cos^2\psi_{ij} - {}^1/_3) \tag{16}$$

where r_{ij} is the distance between dipole centers, and ψ_{ij} is the angle between the cylindrical axes of the dipoles. Interactions involving quadrupoles, octupoles, etc. are neglected. The parameter C is a positive potential constant serving as a measure of the intensity of interactions between a pair of dipoles. In general, C is very weakly dependent on the temperature.

The main idea of the Maier and Saupe theory is the replacement of the sum of interactions between a dipole i and other dipoles in the system by the interaction between the dipole i and the molecular mean field created by the remaining dipoles. Assuming that the dipole system has the cylindrical symmetry axis, averaging $\cos^2\psi_{ij}$ with respect to orientations of the dipole j but constraining the summation with respect to j to the nearest neighbors of the dipole i, Maier and Saupe have obtained the energy ϵ of interaction between a dipole and the molecular mean field as

$$\epsilon = -z_c C r_*^{-6} s P_2(\cos\psi) \tag{17}$$

where z_c is the number of first neighbors surrounding a given dipole, r_* is the average interdipole distance, and ψ is the angle between a given dipole and symmetry axis of the system. The coefficient $z_c C r_*^{-6}$ is a measure of the strength of the interaction between a dipole and molecular mean field. In the Flory and Ronca[4] theory it is assumed to be proportional to the concentration θ and the average length $\bar{\eta}$ of hard sequences. Hence, the ratio $\theta/\tilde{T}$, expressed in kT units, is the measure of the energy of interaction between a unit rigid sequence and the molecular orienting field. The parameter X, defined by eq 15, retains its meaning; it is related to the lowest value of energy where the LC-rich phase appears.

For $X = 0$ we see in Figure 1 two minima of the Helmholtz function, corresponding to the isotropic ($s = 0$) and LC ($s > 0$) phase. For $X < 0$ there is only one stable phase, namely the isotropic phase with $s = 0$. For $X > 0$ we are also away from the LC–i equilibrium, and the only stable phase is the orientationally oriented one.

Experiment, more accurately, scanning electron micrographs of fracture surfaces, shows[19,20] that nearly spherical *islands* of the orientationally oriented phase appear in the LC-poor matrix. We recall rule 4 of the formation of hierarchical structures:[20] the structure of the smaller entity (such as a single molecule) determines the size, shape, and structure of a larger entity (such as a LC phase). We recall also rule 5:[20] assembling entities in a specified way can achieve properties which a system of *un*assembled entities does not have. This clearly applies to the island formation. Figure 1 shows how achieving specified assembly structures (here isotropic and orientationally ordered phases) depends also on parameters displayed in eq 15, that is, the concentration and temperature.

5. Computation Procedure

As mentioned before, the system is described by three model parameters $\bar{y}$, $\bar{\eta}$, and s and by two physical parameters θ and $\tilde{T}$. The variable $\bar{y}$ can be replaced by the variable γ as defined by eqs 6 and 7; for simplification of numerical calculations in the following we shall use γ. On the other hand, the parameter $\bar{y}$ does not have a *simple* experimental interpretation, this by contrast to $\bar{\eta}$ and s. Information on $\bar{\eta}$ can be obtained from parameters which control the synthesis; s is accessible experimentally, for example, from measurements of birefringence, by the ^{2}H NMR method, or from fluorescence spectra; these methods are reviewed in ref 21.

For numerical calculations, eqs 7 and 13 will be used in the following form:

$$G_j(\gamma,\bar{\eta},s,\tilde{T};\theta) = 0 \qquad j = 1\text{–}3 \tag{18}$$

where

$$G_1 \equiv \bar{\eta}(1-\theta)\ln(1-Q) + \bar{\eta}Q + \theta[\ln f_1 + \theta s\tilde{T}^{-1}(1-s/2)] \tag{19}$$

$$G_2 \equiv \gamma + \frac{4\bar{\eta}}{\pi}\ln(1-Q) \tag{20}$$

Here, Q is given by eq 6; the ratio $\bar{y}/\bar{\eta}$ appearing in (6) can be written as[15]

$$\bar{y}/\bar{\eta} = \frac{4}{\bar{\eta}}\langle\sin\psi\rangle = \frac{4}{\pi}\frac{f_2}{f_1} \tag{21}$$

In theories based on the mean-field approach the intensity of the molecular mean field depends on the orientation parameter s; hence the distribution function of segment orientations is parametrized by s (see eq 8). Therefore, the theory has to incorporate the self-consistency equation $G_3 = s - \langle P_2 \rangle = 0$. Here G_3 is of the form:

$$G_3 \equiv \frac{2}{3}(1-s) - \frac{f_3}{f_1} \qquad (22)$$

Thus, we have the system of eqs 19, 20, and 22, four variables $\gamma, \bar{\eta}, s, \tilde{T}$, and a fixed parameter θ. The equations can be resolved using the Flory–Ronca or Newton–Raphson procedure. The Flory–Ronca algorithm chooses to specify γ and solve for s, $\bar{\eta}$, and $\tilde{T}$, with fixed θ. For using the Newton–Raphson algorithm we assume values of $\bar{\eta}$, then s, γ, and $\tilde{T}$ are calculated.

As noted in section 4, we are interested not only in the LC–i phase coexistence but also in the regions of the phase diagrams surrounding that coexistence, that is, the regions with $X > 0$ and $X < 0$ (see eq 15). Those regions can be dealt with by using the Landau approach.[16] From equation $G_3 = 0$ we conclude that for $s = 0$ the parameter $\gamma = 0$. Expanding the reduced Helmholtz function $\tilde{A}$ given by eq 5 in a power series of the order parameter s about $s = 0$ and using eq 7, we obtain $\tilde{A}$ of the form of eq 14, where

$$A_2 = [1.56\bar{\eta}\theta(\theta/\tilde{T}) + 100 - 20(\theta/\tilde{T})]\theta(\theta/\tilde{T})10^{-2} \qquad (23)$$

$$A_3 = [(1.95\theta + 8.20)\bar{\eta}\theta - 28.57]\theta(\theta/\tilde{T})^3 10^{-3} \qquad (24)$$

Hence, we can calculate $\bar{\eta}$ and $1/\tilde{T}$ as functions of A_2 and A_3; the hierarchy of eqs 18 becomes

$$G_j(\gamma, s, A_2, A_3; \theta) = 0 \qquad j = 1\text{–}3 \qquad (25)$$

We are particularly interested in the lowest concentration $\theta_{\mathrm{LC\ limit}}$ at which LC islands appears in a flexible matrix[15] and the parameters pertaining to that limit. In terms of the parameters of eq 14, the respective conditions are

$$A_2 = 0 \quad \text{and} \quad A_3 = 0 \qquad (26)$$

We are also interested in the opposite end of the LC–i coexistence, when the isotropic phase is completely unstable with respect to anisotropic ordering and disappears. For this case we have

$$A_2 = 0 \quad \text{and } A_3 \neq 0 \qquad (27)$$

From eqs 23, 24, and 26 we have in the immediate proximity of the $\theta_{\mathrm{LC\ limit}}$ concentration

$$\tilde{T}_{\mathrm{LC\ limit}} = \theta(\theta + 3.07)/5(\theta + 4.21) \qquad (28)$$

$$\bar{\eta}_{\mathrm{LC\ limit}} = 14.65/[\theta(\theta + 4.21)] \qquad (29)$$

In the above equations θ appears without an index, since it is the choice of θ which defines the limiting state in terms of other variables ($\tilde{T}_{\mathrm{LC\ limit}}$, $\bar{\eta}_{\mathrm{LC\ limit}}$).

6. Results

The dependence between $\tilde{T}_{\mathrm{LC\ limit}}$ and θ is shown in Figure 2. For low θ we find low values of $\tilde{T}_{\mathrm{LC\ limit}}$ of the anisotropic–isotropic transition LC–i. That is, the LC–i transition temperature tends to zero for the system without LC sequences. This is reasonable: the vanishing of the more rigid species, that is, of the source of anisotropy, determines that the system must be deeply frozen for an

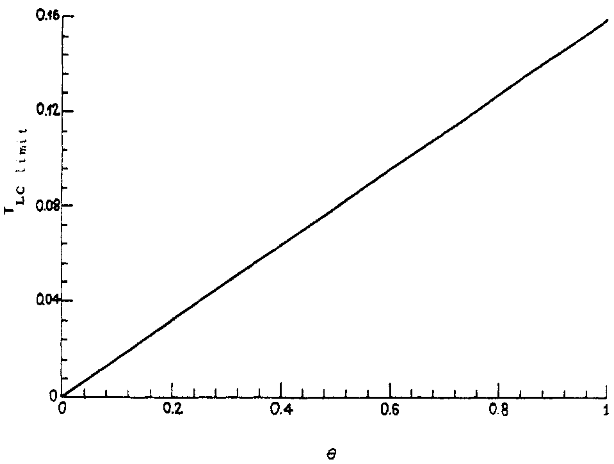

Figure 2. $\tilde{T}_{\mathrm{LC\ limit}}$ as a function of the concentration θ.

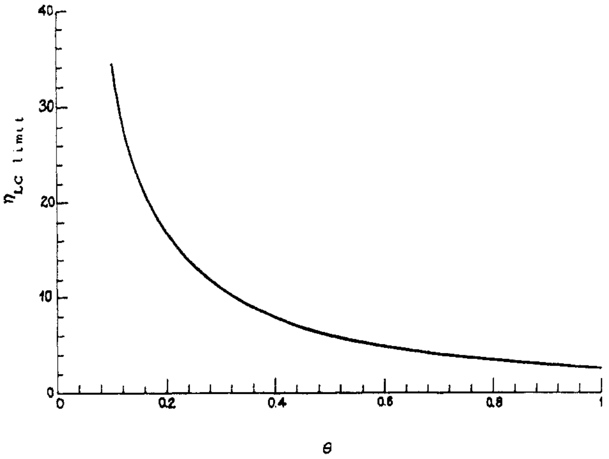

Figure 3. $\bar{\eta}_{\mathrm{LC\ limit}}$ as a function of the concentration θ.

ordering to take place. We find $\tilde{T}_{\mathrm{iso\ limit}} = 0.16$. Here $\tilde{T}_{\mathrm{iso\ limit}}$ represents the end of the LC–i coexistence range opposite to $\tilde{T}_{\mathrm{LC\ limit}}$. In other words, for values of $\tilde{T} > 0.16$ the only stable phase is the orientationally disordered isotropic one. This situation stems from a disorientation entropic mechanism: the system chains become more and more coiled with a temperature increase.

Analogous dependence for $\bar{\eta}_{\mathrm{LC\ limit}}$ vs θ is shown in Figure 3. In this case the anisotropic–isotropic transition is impossible for $\bar{\eta} < 2.81$; then only the isotropic phase is observed (see again Figure 1). The result can be explained by a competition between the entropic mechanism, which enhances coiling of macromolecules, and the anisotropic interaction mechanism, which enhances their parallel orientation. Following Samulski,[22] we divide LCs into PLCs and monomer liquid crystals (MLCs), irrespective of whether the latter can or cannot polymerize. We now find that the existence of $\bar{\eta}_{\mathrm{LC\ limit}}$ is characteristic for PLCs. In MLCs, with relatively stronger interactions, the liquid crystallinity is not limited by the length of the hard rod molecules.[23–25]

With a decrease of θ, the axial anisotropy of hard rods has to increase, so that the anisotropic–isotropic phase transition would be still possible. This is why we find an increase of $\bar{\eta}_{\mathrm{LC\ limit}}$ to infinity for θ tending to zero.

We now consider solutions of eq 25 with respect to s as a function of the parameter X defined by eq 15. The results for a series of θ values in 0.1 intervals are shown in Figure 4. While Figure 1 was qualitative, so as to show the kinds of behavior which are possible, we now have quantitative results for $X > 0$. Equations 18 are equivalent to eqs 25 and have a trivial solution for $s = 0$: $G_3 = 0$ gives

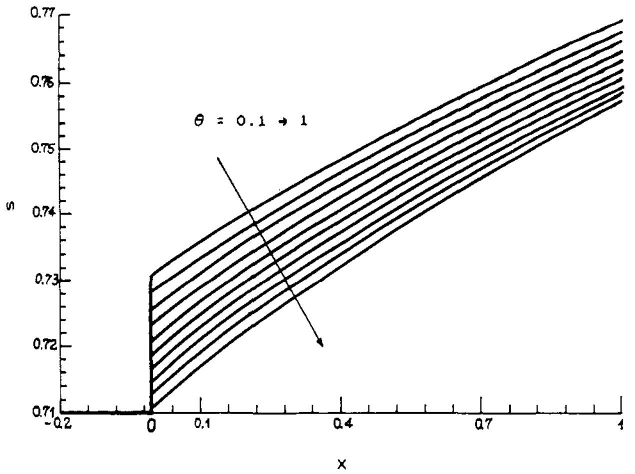

Figure 4. The order parameter s as a function of X as defined by eq 15 for various values of the concentration θ. The parameter θ is varied in 0.1 intervals. For $X < 0$ the isotropic phase is stable. For $X = 0$ the anisotropic–isotropic phase transition is observed. For $X > 0$ the isotropic phase is completely unstable with respect to anisotropic ordering.

$\gamma = 0$, thus $Q = 0$, $G_2 = 0$ and $G_1 = 0$, independent of values of parameters θ and $\tilde{T}$. Of course, for any regions of values of θ and $\tilde{T}$ the trivial solution does not have physical sense. We must find different and nontrivial solutions. Unfortunately, the hierarchy of equations 18 has more than one nontrivial solution. Using Matheson–Flory or Newton–Ralphson procedures, we do not have a simple criterion for the choice of the appropriate solution. Therefore, we use the coefficients A_2 and A_3 to obtain the physically appropriate solutions.

The description of our system in the stable anisotropic phase is given by solutions of eqs 25 for A_2 tending to zero. For positive values of X we have $s_{\mathrm{LC\ limit}} = 0.71$ and $s_{\mathrm{iso\ limit}} = 0.73$. On the other hand, for $X = 0$ eqs 25 have the solution $s = 0$. Thus, we can say that for values near $X = 0$ the bifurcation point, known to exist in LC systems,[23] is observed. Taking X as negative, eq 25 has a solution for a positive value of s and, as discussed above, a solution for $s = 0$. However, for the positive s near $X = 0$ the coefficient A_3 does not change its sign at $X = 0$; this change is needed, in the Landau theory terms, for the isotropic–anisotropic transition. We conclude, therefore, that the physically reasonable solutions are those displayed in Figure 4.

For small positive values of X, the parameter s is only weakly affected by varying θ. For larger X, the parameter s is practically independent of θ; see Figure 5. For $\theta = 0$ the system of equations (18) or, equivalently, equations (25) is satisfied by identity with respect to all variables with finite values, but the equations do not give information on the physical state of the system. However, for $\theta = 0$, $\tilde{T}$ decreasing to zero, and $\bar{\eta}$ tending to infinity, it is possible to find a formal solution of eqs 18 with a finite s. The result is in accordance with the results for $\tilde{T}_{\mathrm{LC\ limit}}$ and $\bar{\eta}_{\mathrm{LC\ limit}}$. Therefore, for $\theta = 0$ the choice of $s = 0$ is reasonable for the physical reasons discussed above, while it is mathematically valid as well.

An inspection of Figure 4 shows also that, for a positive value of X, the parameter s decreases with an increase of θ. At first sight this result appears unexpected. To understand it, return to the definition (15) of X. The term $(\theta/\tilde{T})_{\mathrm{LC\ limit}}$ is a decreasing function of θ; hence, per definition, X increases with θ. For a constant value of $\tilde{T}$, Figure 4 shows that the orientation parameter s is an increasing function of the concentration of rigid sequences θ.

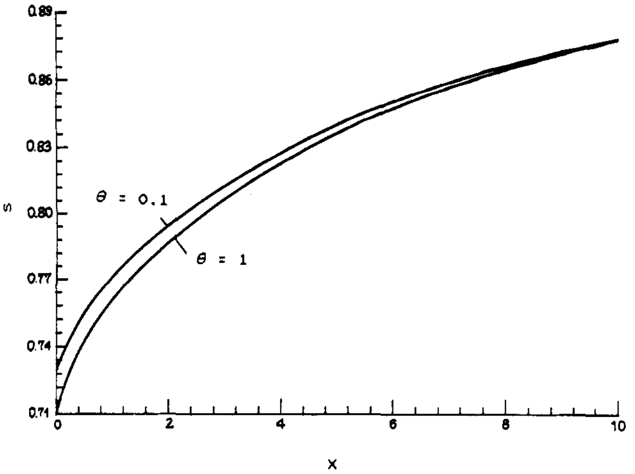

Figure 5. Order parameter s vs X for larger values of X.

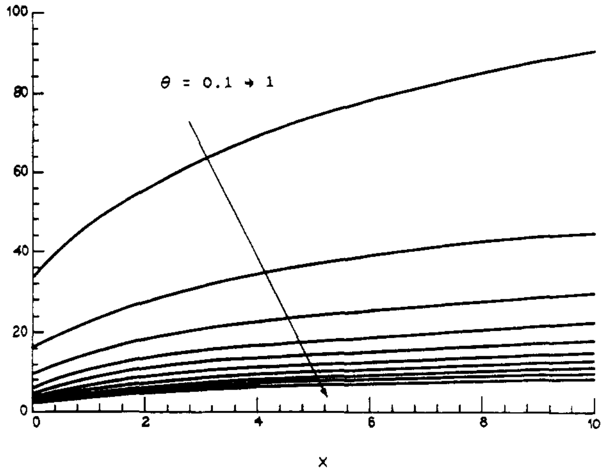

Figure 6. A master plot for the dependence between the length of rigid sequences $\bar{\eta}$ and the parameter X for various values of the LC concentration θ for the system in an orientationally ordered phase; X and θ as in Figure 4.

In Figure 6 we show a master plot of the dependence of $\bar{\eta}$ on X for various values of θ. The dependence is obtained from eq 24 for values of A_3 obtained from eqs 25. The parameter X is proportional to the quantity $\theta\bar{\eta}T^*/\tilde{T}$; see eqs 9 and 15. Inspection of Figure 6 shows that $\bar{\eta}$ is a decreasing function of θ. This is expected, since $\bar{\eta}$ increases if the measure of the intensity of interactions T^* decreases; moreover, $\bar{\eta}$ goes symbatically with the temperature $\tilde{T}$. This can be seen when we write $\bar{\eta} = f(X) \sim XT/\theta T^*$, where f is the function shown in Figure 6. The above results are in accordance with the results for the phase coexistence line presented in Figures 2 and 3 (for $\bar{\eta}_{\mathrm{LC\ limit}}$ and $\tilde{T}_{\mathrm{LC\ limit}}$ vs θ). They are also reasonable from the physical point of view. Namely, for small numbers of LC segments in the system and for weak interactions between them, the length $\bar{\eta}$ must be large to create a stable anisotropic phase; by contrast, $\bar{\eta}$ values can be smaller at lower temperatures when an orientationally ordered phase can be created more easily.

7. Discussion and Conclusions

We have considered the monodisperse PLC system of macromolecules, with macromolecules consisting of flexible and relatively rigid parts. We have used the Flory–Matheson lattice model with incorporation of potential orienting interactions between rigid sequences. Using the parameters of the Landau theory of LC systems,[16] we have derived a procedure for the range between the LC limit and iso limit in which the orientationally ordered and isotropic phases coexist. In the limit of the Landau approximation, a simple criterion for the physical state of the system has been obtained, eqs 23, 24, 26, and 27.

The phase diagrams for the reduced temperature $\tilde{T}$ and the average length of the rigid sequences $\bar{\eta}$ vs concentration of LC segments θ have been shown in Figures 2 and 3. We have found the values $\tilde{T}_{\mathrm{LC\ limit}} = 0.16$ and $\bar{\eta}_{\mathrm{LC\ limit}} = 2.81$, where for $\tilde{T} > \tilde{T}_{\mathrm{LC\ limit}}$ and $\bar{\eta} < \bar{\eta}_{\mathrm{LC\ limit}}$ a stable anisotropic phase cannot exist. The behavior of the system is understandable in terms of competition of two molecular mechanisms: coiling of macromolecules by thermal–entropic forces and the alignment induced by the anisotropic orienting interactions. As the result, we have found that $\bar{\eta}$ is larger for PLC than for MLC systems.

The dependence of the orientation factor s on the reduced parameter X, for various concentrations θ of the hard segments, has been shown in Figure 4. For values $X < 0$, an isotropic stable phase with respect to anisotropic ordering is found; for $X = 0$ we have the isotropic–anisotropic transition, while $X > 0$ values correspond to a stable anisotropic phase. For $X < 0$ the orientation parameter $s = 0$. At $X = 0$ the bifurcation point is observed; at that point we have two coexisting phases: isotropic with $s = 0$ and anisotropic with $s = s_{\mathrm{LC\ limit}}$. Values of $s_{\mathrm{LC\ limit}}$ are about 0.72 and they are very weakly controlled by varying the concentration θ. For $X > 0$ values of s increase with increasing X; for example, for $X = 10$ the orientation parameter $s = 0.89$. For large positive X the parameter s is practically independent of the concentration θ and tends to unity.

In the range of the anisotropic–isotropic phase coexistence, the values of s vary between $s_{\mathrm{LC\ limit}} = 0.71$ and $s_{\mathrm{iso\ limit}} = 0.73$. Analogous values of the parameter $\theta/\tilde{T}$ are between 6.40 and 6.81. In the Maier–Saupe theory of LC systems[24,25] the value of s is equal to 0.44 and the value of the interaction parameter analogous to $\theta/\tilde{T}$ is equal to 4.55. However, any comparison of the results for PLC systems presented here and the Maier–Saupe results for MLC systems must be treated cautiously. The Maier–Saupe theory is not a lattice theory. Their system consists of unconnected hard unit segments only; there are no chains of connected segments nor are there any flexible sequences. Thus, in terms of the theory presented here, the concentration θ is equal to 1 and the anisotropy of a rigid sequence, which is characterized by the parameter $\bar{\eta}$, is equal to unity. As discussed above, the anisotropy of rigid sequences needed for liquid crystallinity in the PLC system must be larger. As a consequence, the repulsive anisotropic interactions on contact are stronger in PLC than in MLC systems. Hence, the limiting value of $s_{\mathrm{LC\ limit}}$ must be larger in PLC systems than in MLC systems. Moreover, in PLCs we need to take into account a *collective* response of orientations in the presence of a molecular mean field; the collectivity stems from the connectivity of sequences in chains and exerts its influence by increasing the $s_{\mathrm{LC\ limit}}$. An analogous situation is observed for electrically active PLC systems, in which the collective response of mesogenic dipole units to the presence of the external electric field leads to much larger values of total dipole moment than that for LC systems of unconnected dipoles.[26] On the other hand, in experiments[27] and in computations pertaining to those experiments,[18] we find large values of s much closer to 0.72 rather than to 0.44.

The dependence of $\bar{\eta}$ on X for various values of θ has been shown in Figure 6. For the system in a stable anisotropic phase, the parameter $\bar{\eta}$ is a decreasing function of the concentration θ and of the interaction intensity T^*, and it is inversely proportional to the temperature T. These results are in accordance with results obtained for the system at the border between the isotropic and anisotropic phases shown in Figures 2 and 3.

We have considered here only monodisperse systems, while real PLC systems are polydisperse. The question how does polydispersity affect the behavior of PLC systems near the orientationally ordered–isotropic transition point will be considered in the following paper in this series.

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