Rod-to-Coil and Order–Disorder Transitions in Nematic Polymers

Clive A. Croxton

Department of Mathematics, University of Newcastle, Shortland, NSW 2308, Australia.

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ABSTRACT: We determine the nematic order parameter S of a linear, semiflexibly linked sequence of rigid rods with respect to an external director field as a function of length, reduced temperature, and chain stiffness on the basis of the iterative convolution (IC) approximation. The mean-square length $\langle R_N^2\rangle$ and the mean-square radius of gyration $\langle S_N^2\rangle$ are also determined as a function of these parameters. We find that all systems exhibit a pronounced order–disorder transition over a narrow range of reduced temperature, although this does not necessarily imply a rod–coil transition. Indeed, the distinction between the order–disorder transition and the rod–coil transition is at its most marked for perfectly flexible systems for which S shows a pronounced first-order phase transition while $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ remain constant throughout. With increasing flexibility $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ show a progressively more gradual transition to the extended state with decreasing temperature, and although the *onset* of the transition coincides with that of the order parameter, only for the stiffest systems can an unequivocal rod–coil transition be said to occur. Although the number of hairpins cannot be determined in this analysis, a qualitative discussion in terms of hairpins is presented. The IC estimates are in good agreement with Monte Carlo results presented in a subsequent publication.

Introduction

Considerable interest has developed in the extension of our understanding of conventional low molecular weight mesogenic systems to polymeric mesophases which offer the possibility of intriguing new phenomena associated with the additional internal degrees of freedom available within the molecule itself. Of the two principal classifications of liquid crystal polymers, main chain and side chain, the latter are probably of more interest to the LC materials chemist as alternative substrates for electrooptical displays, while a major component of the former classification are biological in origin, consisting of alternating sequences of helical and flexible polypeptide: indeed, Jähnig[1] was one of the first to discuss such systems in the context of the nematic environment of membrane structure. A second form of backbone structure consists of a linear sequence of stiff and less stiff sections or a uniformly stiff (but not rigid) sequence that is characterized by a persistence length l and as such is termed a wormlike chain having its flexibility distributed homogeneously along its length. Flory[2] modeled such a system as a sequence of flexibly connected rigid rods each of length l in which case chain flexibility is localized at the junction points; subsequent mesogenic behavior was then treated as for conventional low-weight rigid-rod systems whose LC characteristics are determined by their axial ratio.

Analyses of the wormlike chain in the presence of an external potential presented by Jähnig, and more recently by ten Bosch et al.,[3] were essentially perturbative in their approach and as such were incapable of describing important qualitative characteristics of the system such as the singular approach to the rod limit at low temperatures, with the associated development of hairpin states (de Gennes[4]). A treatment that embodies both the weak and strong limits of nematic potential has been developed by Warner et al.[5] who find that the problem is equivalent to the diffusion of the head of a unit tangent vector to the chain over a unit sphere, and may be described by a spheroidal wave equation whose eigenvalues and eigenvectors are determined in the limits of weak and strong nematic potential. More recently Vroege and Odijk[6] have investigated induced chain rigidity on the basis of a nonlinear integrodifferential equation first formulated by Khokhlov and Semenov,[7] again for wormlike chains interacting via hard-core repulsions in the second virial approximation.

In a variety of earlier papers (Croxton[11,12]) the iterative convolution (IC) description of polymer configuration was presented. In those papers the configurational properties of fully self-interacting polymer sequences were determined for a wide variety of polymer geometries (linear, ring, star, ladder) under various degrees of confinement (surfaces, occlusions) both in the absence of solvent and as a function of solvent quality. In addition to the geometrical properties, a priori determinations of the polymer scattering function were also presented on the basis of the IC technique. In all cases the only input was the specification of the intersegmental pair potential $\Phi(ij)$ between each pair of segments i,j within the system that may itself be homo- or heterogeneous. The objective of the IC treatment was to provide a unified approach to polymer structure and scattering, and certainly comparison with Monte Carlo estimates of the various quantities appears to support the IC technique as a successful theory of polymer configuration.

Theory

Here we extend the iterative convolution technique[11] to the description of linear semiflexible nematic chains in which the coupling of the internal degrees of freedom causes a change in chain statistics and the development of orientational order. As such, the present analysis represents the *orientational* counterpart to previous IC descriptions that were based essentially upon spatially dependent interactions between the segments. We model the chain as a sequence of unit rods (Figure 1a), flexibly connected such that the bend potential between adjacent rods is given by

$$\begin{aligned}\Phi(\theta_{i,i+1}) &= 0 \qquad \theta_{i,i+1} \le \theta_{\max}\\ &= +\infty \qquad \theta_{i,i+1} > \theta_{\max}\end{aligned} \tag{1}$$

Clearly, the specification of the range $\theta_{\max}$ specifies the flexibility of the sequence, becoming a stiff rod when $\theta_{\max} = 0$ and totally flexible when $\theta_{\max} = \pi$. The unit rods provide a natural measure of the persistence length l, and to this extent our model coincides with Flory's description.[2]

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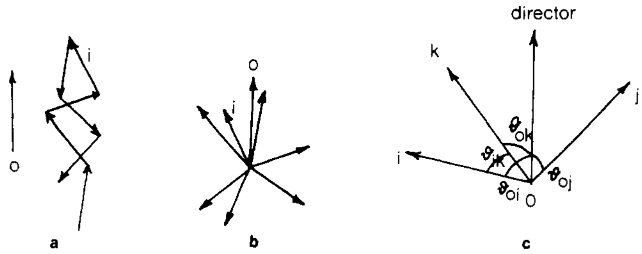

Figure 1. (a) Linear nematic polymer comprising N unit rods, each of which has its orientation with respect to an external director field **0** specified by (θ_i, ϕ_i). (b) An equivalent representation of the polynematic sequence shown in (a). (c) The vectors and associated angles involved in the convolution integral eq 6.

Since we are concerned essentially with the *orientational* features of the system, and in particular the orientation of the coupled rods with respect to an external director field, it is convenient to represent the system as a bunch of unit vectors as shown in Figure 1b. If we designate the director by the vector **0**, then given that the system is cylindrically symmetric about **0** ($\Phi(\phi_{0i})$ = constant, where ϕ_{0i} is the rotational displacement of the ith rod about the vector **0**), we need only to determine the angular distribution functions $Z(\theta_{ij}|N)$. The distribution $Z(\theta_{0j}|N)$ describes the orientation of the jth rod with respect to the director **0**, while $Z(\theta_{ij}|N)$ describes the relative orientation of rods i and j, given, of course, that they are in a coupled sequence of N rods subject to an external director field. Coupling between rods to the director field is discussed below (eq 3).

The *order parameter* S for the set of N rods in the sequence with respect to the "external" vector "0" is defined in terms of the orientational average $\langle\ \rangle$ along the chain

$$S = \frac{1}{N}\sum_{j=1}^{N} S_j = \frac{1}{N}\sum_{j=1}^{N}\langle(3\cos^2\theta_{0j} - 1)/2\rangle = \frac{1}{N}\sum_{j=1}^{N}\int_{1}^{-1}(Z(\cos\theta_{0j}|N) \times (3\cos^2\theta_{0j} - 1)/2)(\mathrm{d}\cos\theta_{0j}) \quad (2)$$

where S_j is the order parameter of the jth rod, and with a knowledge of the $Z(\cos\theta_{0j}|N)$ the order parameter may then be readily determined. This is a trivial extension of the conventional definition of the orientational order parameter for a single rod.[10] If we do not distinguish between parallel and antiparallel alignment with respect to the director, then S varies between +1 and $-1/2$, corresponding to perfect alignment along and perpendicular to the director field, respectively. $S = 0$ corresponds to a random distribution of the rods with respect to the director: $Z(\cos\theta_{0j})$ = constant.[17] A clear distinction should be made between the "external" order parameter arising from the degree of rod alignment with respect to an external director and the "internal" order parameter relating to the alignment of the rods with respect to the long molecular axis of the sequence. (Note that by molecular axis we do *not* mean the chain backbone contour.) The distinction is perhaps clearest for a fairly stiff sequence in which there is an intrinsically high degree of internal alignment of the rods along the molecular axis and a correspondingly high value of the internal order parameter. The external order parameter with which we are concerned here, however, may nevertheless remain small or even zero for random orientations of the molecular axis with respect to the external field.

It may be argued that the internal order parameter is sensitive to chain stiffness and that the "external" function with which we are concerned here is only weakly dependent upon the stiffness of the chain. One can imagine progressively stiffening a linear sequence of rods and observing the order parameter. Ultimately the chain reduces to a single rigid rod for which stiffness has no significance, and we must conclude in this case that stiffness and chain length can have no bearing upon the "external" order parameter S. Similar reasoning may be applied to a perfectly flexible chain resulting in the same conclusion. We shall return to this point later. In the case of simple rigid linear nematics an association between the molecular axis, the director, and the order parameter is more easily made. Here, however, molecular flexibility introduces an additional complication giving rise to some dispute in the literature as to whether there is or is not close identification of the director with the molecular axis (see, for example, de Gennes,[4] Warner et al.,[5] and Meyer[8]). Meyer[8] catalogs numerous qualitative differences between the two possibilities, the most notable being the projected divergence of the splay constant with molecular length in the case of close coincidence of the director and the molecular axis.

It should be said that Warner et al. specifically distinguish between the two possibilities and emphasize that the molecular axis (chain backbone) in their wormlike model is *not* to be identified with the director. Nevertheless, the chain is visualized as meandering about the director, and it does appear that the mean molecular axis *does* remain in close registry with the director. This being the case, with no prospect of an orientational distribution of the mean molecular axes with respect to the director, Warner et al. are in fact determining the internal order parameter discussed above, and this will be sensitive to chain rigidity. To that extent these authors are calculating a different order parameter to that being considered here.

We work in the mean field approximation of Maier and Saupe,[9] who in their original presentation assumed that the stability of the nematic phase arises from the dipole–dipole part of the anisotropic dispersion forces which, in conjunction with an assumption of cylindrical symmetry about the preferred axis and in the absence of polarity and steric interactions, yields

$$\Phi(\theta_{0i}) = \frac{-AS}{2V^2}(3\cos^2\theta_{0i} - 1) \quad (3)$$

for the orientation dependent part of the potential energy of the ith rod with respect to the director. V is the molar volume, A is a constant taken to be independent of pressure, volume, and temperature, and S is defined above. In fact, the change of volume across the nematic–isotropic transition is so small (Chandrasekhar[10]) that for present purposes we may regard it as constant and absorb it into the parameter A; moreover we prefer to work in terms of the reduced potential parameter $A^* = A/kT$ throughout. Other workers[16] have also presented justifications for the use of the original Maier–Saupe representation of the orientational potential adopted here, although we should point out that Vroege and Odijk[6] have recently criticized this approach.

It is not appropriate here to review the iterative convolution approach; for details of the technique we refer the reader to the literature (Croxton[11]). Basically, the technique permits the description, in terms of the spatial probability distributions $Z(ij|N)$, of the configurational properties of self-interacting polymer systems in which the only input specification is the set of pairwise interactions operating between each pair of monomers,

i,j. Thus, systems of nonlinear geometry, the incorporation of boundaries, and other confinements, solvents, external fields, etc. may be readily described, and as such the theory provides a unified statistical mechanical approach to the description of configurational and scattering properties of homo- and heteropolymeric systems. However, all previous applications of the technique have been based on central pairwise *radial* interactions while this is its first application to orientationally dependent functions. Essentially, the IC integral equation relates the spatial probability distribution $Z(ij|N)$ between any two monomers i,j within the N-mer in terms of the propagation of correlation via all other monomers in the sequence. It may then be shown[11] that to a good approximation

$$Z(ij|N) = H(ij) \prod_{k=0\neq i,j}^{N}{}' \int Z(ik|N)\, Z(kj|N)\, \mathbf{dk} \qquad (4)$$

$$H(ij) = \exp(-\Phi(ij)/kT) \qquad (5)$$

where $\Phi(ij)$ is the interaction potential operating between segments i and j and $\prod'$ is the geometric mean of the $N - 2$ convolution integrals arising from $1 \leq k \neq i,j \leq N$. A qualitative understanding of eq 4 may be gained by regarding $Z(ij|N)$ as comprising the "direct" Boltzmann distribution $H(ij)$, mediated in the field of the neighboring segments given by the geometric mean of the product of the normalized convolution integrals. For the present problem the spatial distributions take the form of angular functions and the IC equation takes the form[17]

$$Z(\cos\theta_{ij}|N) = H(\cos\theta_{ij}) \prod_{k=0\neq i,j}^{N}{}' \int Z(\cos\theta_{ik})\, Z(\cos\theta_{kj})\, \mathbf{dk} \qquad (6)$$

where $\mathbf{dk} = \mathrm{d}\phi_{ok}\, \mathrm{d}(\cos\theta_{ok})$ and the chain–director function

$$H(\cos\theta_{oj}) = \exp(A^*S(3\cos^2\theta_{oj} - 1)/2) \qquad (7a)$$

where the asterisk designates the reduced potential multiplier $A^* = A/kT$. A clear distinction should be made between chain–director functions $H(0j)$ and chain–chain functions $H(ij)$. The chain–chain functions $H(ij)$ are rather more subtle in this orientational problem than in the purely spatial systems considered previously. In fact, the $H(ij)$ must first be determined as the appropriate *convolution of distributions* implied by the flexibility defined in eq 1 for the $|i-j|$ flexible joints between the two rods in question. Thus, for two rods i and j their relative angular distributions are correctly given as the convolution of the intervening angular distributions:

$$H(\cos\theta_{ij}) = \int H(\cos\theta_{i,j-1})\, H(\cos\theta_{j-1,j})\, \mathrm{d}(\mathrm{j}-1) \qquad (7b)$$

Although the deviation from a simple arithmetic addition and renormalization of the rectangular distributions is not great, eq 7b is nevertheless technically correct and, since it is readily evaluated, is used throughout these IC calculations (Figure 2). The $H(ij)$ functions depend sensitively upon both chain flexibility (the "bend" potential, eq 1) and their relative separation, $|i-j|$. This is a fundamental difference for this system compared with homogeneous spatially dependent (as opposed to orientationally dependent) systems in which all $H(ij)$ are identical, regardless of i,j.

The vectors involved in the convolution integral are illustrated in Figure 1c. The integral is evaluated numerically and iteratively for all orientations of the vectors, i, j, and k. It should be noted that the stiffness of the sequence implies maximum permissible angular ranges for the angles θ_{ik} etc., and these are determined as the cumulative sum of adjacent flexibilities specified in eq 1. Thus, the maximum relative angular range between rods i and k is

$$\theta_{ik_{\max}} \leq |i-k|\theta_{\max} \qquad (8)$$

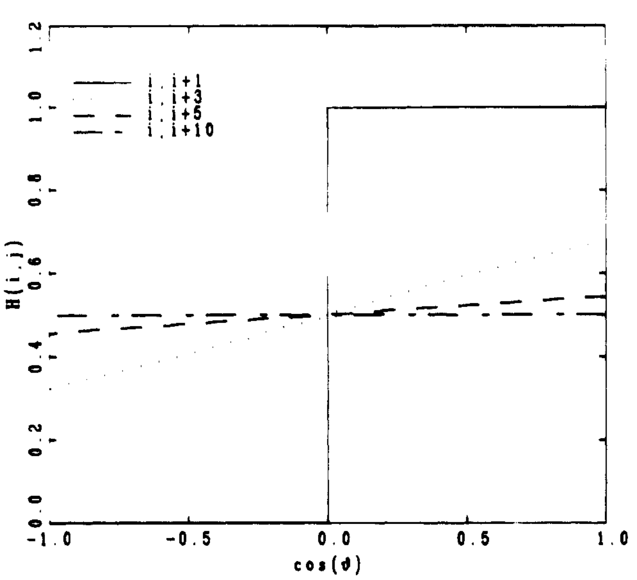

Figure 2. The direct interaction function $H(\cos\theta_{ij})$ as a function of various chain contour separations $|i-j|$ in a sequence having stiffness $\theta_{\max} = 0.5\pi$ (eq 1).

Evaluation of the convolution integral (eq 6) is practicable in real space because of the short range of the functions: the substantially longer ranged integrals in previous applications of the IC technique have been handled by fast Fourier transform techniques.

A further complication in this IC analysis arises from the fact that one of the principal parameters to be determined in this investigation is the order parameter S, yet this function features explicitly in the specification of the orientational interaction (eq 3). In fact S has to be determined self-consistently in the course of the iterative solution of the coupled integral equations, and we seek convergence of both S and the angular distribution functions, the former being related to the latter via eq 2.

The complete set of chain–director ($Z(\cos\theta_{oi}|N)$) and chain–chain ($Z(\cos\theta_{ij}|N)$, $i \neq j \neq 0$) orientational distributions are determined via eq 6 on the basis of which the order parameter (eq 2) and the mean-square chain length $\langle R_N^2\rangle$ may be determined. This latter quantity is defined as

$$\langle R_N^2\rangle = N + 2\sum_{i<j}\langle\cos\theta_{ij}\rangle \qquad (9)$$

Similarly, the mean-square radius of gyration $\langle S_N^2\rangle$ of the sequence may be determined:

$$\langle S_N^2\rangle = \frac{1}{(N+1)^2}\sum_{i\leq j}\langle R_{ij}^2\rangle$$

$j = i$ is included because $\langle R_{ij}^2\rangle$ is the mean-square length of the subchain consisting of links (not segments) i through j.

Results and Discussion

In this section we present the results of the IC calculations although frequent comparisons will, of course, be made with other analyses wherever possible. Unfortunately, however, there is some diversity in the literature regarding the basic parametric description of the prob-

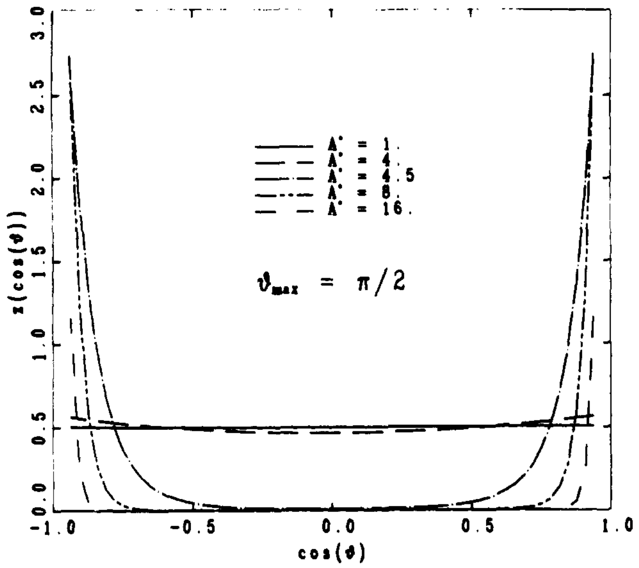

Figure 3. The normalized orientational distribution function $Z(\cos\theta_{oi}|N)$ determined on the basis of the IC approximation as a function of A^*, for $i = 5$ and $N = 10$. Note the transition in the form of the distribution over the range $4.0 < A^* < 4.5$. Distributions are shown for a chain flexibility of $\theta_{max} = \pi/2$.

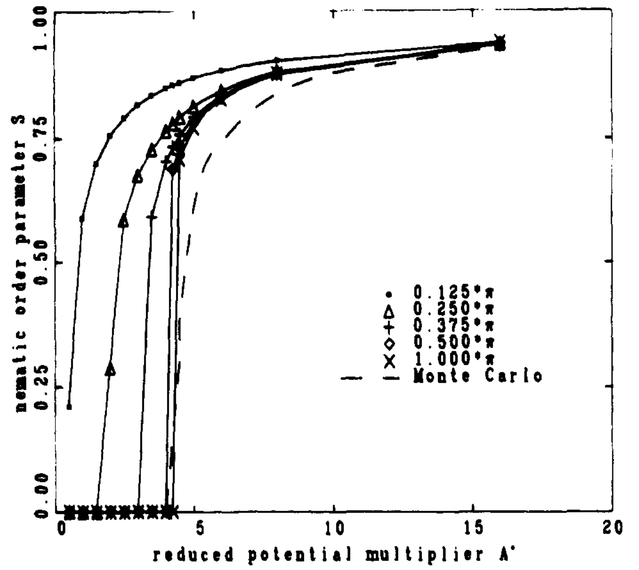

Figure 4. The order parameter curves S as a function of reciprocal temperature A^* and chain stiffness $0.125\pi \leq \theta_{max} \leq \pi$ for chains of length $N = 10$. The Monte Carlo result for chains of length $N = 10$ and $\theta_{max} = \pi$ is also shown.

lem, even including the specification of the mean field interaction operating within the system, and accordingly qualitative comparisons only are possible in the majority of cases. Clearly, direct comparison of the IC results with the MC data would appear to form the most appropriate basis for discussion, and this we shall do in a subsequent publication. We anticipate the comparison, however, with the observation that in general the qualitative agreement between the present calculations and the MC simulations is good to excellent, and the IC technique again appears to provide a sound semiquantitative description of this polymeric system.

In Figure 3 we show $Z(\cos\theta_{oi}|N)$ as a function of reciprocal temperature A^* for $i = 5$ and $N = 10$ for chains of stiffness $\theta_{max} = \pi/2$. This function corresponds to the orientational distribution of segment 5 within the 10-mer relative to the director field: distributions $Z(\cos\theta_{oi}|10)$ $(i \neq 5)$ for other segments in the sequence show a marginal relaxation in their form as the ends of the chain are approached but do not differ significantly from the distributions shown here. The most striking feature of these distributions is their very sharp transition from a uniform spherically symmetrical orientational distribution for $A^* \lesssim 4.0$ to a strongly bimodal function at $A^* \gtrsim 4.5$, suggesting a reduced reciprocal nematic–isotropic transition temperature, $A_{NI}^* = (T_{NI}^*)^{-1}$, somewhere between these two values. Such distributions are fully consistent with the development of hairpins, although these latter cannot be explicitly resolved on the basis of the IC technique. Indeed, at large A^*, corresponding to temperatures well below the transition, the orientational distribution reflects the almost perfect alignment of the monomers along the director field for all stiffnesses, while at higher temperatures an almost uniform orientational distribution confirms that a thermotropic nematic–isotropic transition has taken place. These features are confirmed on the basis of the Monte Carlo determinations, although the latter estimates suggest a somewhat more relaxed orientational distribution for a given specification of N, A^*, and θ_{max}. This discrepancy is attributed to the approximate nature of the IC technique.

These orientational distributions may now be used to estimate the orientational averages $\langle\cos^2\theta_{oj}\rangle$ and $\langle\cos\theta_{ij}\rangle$. On the basis of a knowledge of $\langle\cos^2\theta_{oj}\rangle$ the order parameter of the chain with respect to the external director may be determined, as defined in eq 2. In Figure 4 we plot the family of order parameter curves as a function of chain stiffness and reciprocal temperature for $N = 10$. The curves exhibit a number of distinctive features, in particular a pronounced order–disorder transition in the orientational order parameter of the system over a relatively narrow reciprocal temperature range. The transition appears to be first order and located at $A^* \sim 4.5$, which concurs very closely with the original Maier–Saupe estimate for nematic liquid crystalline systems for which $A_{NI}^* = 4.541$.[10]

As we have discussed already, a priori considerations suggest that the location of the transition should vary weakly with stiffness, and indeed, to anticipate the results of our Monte Carlo simulations, this does appear to be the case to within statistical error for the particular choice of flexibility given in eq 1. The somewhat more substantial spread in the location of the transitions on the basis of the IC technique must therefore be considered a real feature of the transition. Certainly we could find no basis for its elimination. It should be said, however, that this conclusion is in marked contrast to the results of Warner et al.[5] and subsequently Wang and Warner[14] who find that the location of the transition varies as the square root of the elasticity modulus ϵ or stiffness: $kT_{NI} \sim (\epsilon)^{1/2}$. No comment is made by these authors regarding perfectly flexible ($\epsilon = 0$) or perfectly rigid ($\epsilon = \infty$) systems, particularly since these systems should reduce to the known result for a single rigid rod. Moreover, the result of Warner et al. appears at variance with the Monte Carlo results to be reported in a subsequent publication. However, the Warner result does appear more consistent with an estimate of the *internal* order parameter, that is, the degree of alignment of the chain along the mean molecular axis, although they frequently reassert that there is *not* a rigid identification of the molecular axis and the director in their treatment and that their order parameter is determined with respect to the director. They also conclude that the transition is length dependent, again at variance with the IC and MC determinations. Both our IC and MC calculations suggest a very weak length dependence for $N \gtrsim 10$.

The discontinuous behavior of the order parameter at

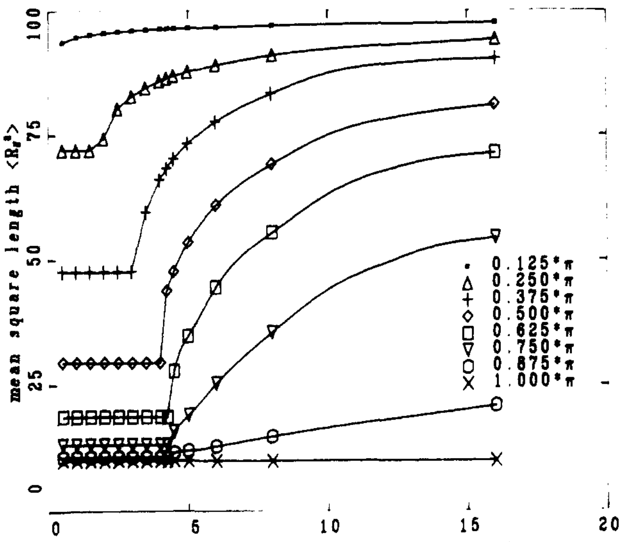

Figure 5. The mean-square end-to-end length $\langle R_N^2 \rangle$ as a function of A^* and chain stiffness $0.125\pi \leq \theta_{\max} \leq \pi$ ($N = 10$).

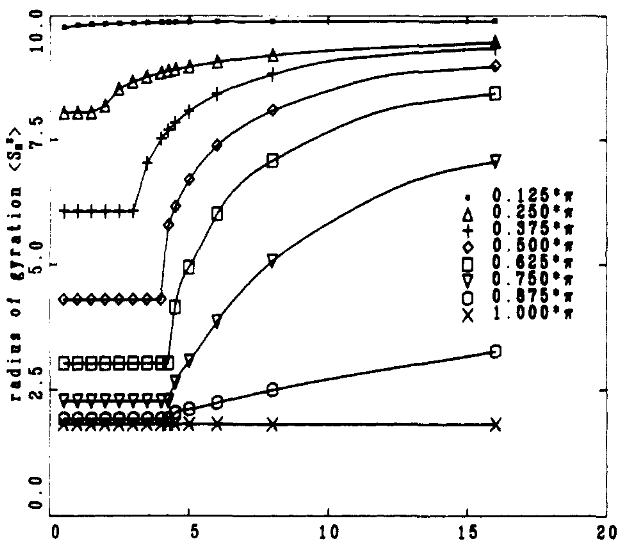

Figure 6. The mean-square radius of gyration $\langle S_N^2 \rangle$ as a function of A^* and chain stiffness $0.125\pi \leq \theta_{\max} \leq \pi$ ($N = 10$).

the transition temperature strongly suggests that the phase transition is first order, even for the relatively short chains investigated here. This appears to concur with the conclusions of Warner et al.[5] but is in disagreement with ten Bosch et al.[3] who obtain a second-order transition. Again, these qualitative features are confirmed by the Monte Carlo determinations. Warner et al. discuss two limiting cases for the evaluation of the order parameter at the transition corresponding to a weak and a strong nematic limit. They find the discontinuity ΔS_{NI} to be 0.755 and 1/3, respectively, while in both cases the transition temperature T_{NI} varies as the square root of the stiffness parameter. Unfortunately both estimates are only to leading order, and there is no guarantee that higher terms will not modify their conclusions. Indeed, further analysis by Wang and Warner[14] shows that higher terms may be significant. Certainly both our IC and MC determinations are inconsistent with this conclusion.

The $\langle \cos \theta_{ij} \rangle$ yield the mean-square end-to-end length $\langle R_N^2 \rangle$ (eq 9) and radius of gyration $\langle S_N^2 \rangle$, both of which are seen to depend sensitively upon chain stiffness and reciprocal temperature A^* (Figures 5 and 6). It is appropriate to observe from the outset that both these quantities depend fundamentally upon the orientation, parallel or antiparallel, of the constituent rod segments. In this respect we anticipate some qualitative differences from the behavior of the order parameter reported above and the dependence of these quantities upon the development of hairpin states.

At high temperatures, corresponding to small values of the reduced potential multiplier A^*, the mean-square length of the sequence corresponds to that of a constrained random walk. Thus, for a chain of $N = 10$ segments $\langle R_N^2 \rangle = 100,(10)$ for $\theta_{\max} = 0,(\pi)$ corresponding to a perfectly stiff and perfectly flexible chain, respectively. For these two limiting flexibilities it is straightforward to show that $\langle R_N^2 \rangle$ *is independent of* A^*, *and* this is confirmed by the IC calculations shown in Figure 5.

For chains of intermediate flexibility the sequences show what is probably best described as an "elongation" with increasing A^*, coinciding with the order–disorder transition. Even for the highest values of A^* investigated, the system cannot be said to have achieved a rodlike state on the basis of estimates of $\langle R_N^2 \rangle$ and $\langle S_N^2 \rangle$ (Figures 5 and 6). Certainly the elongation is a sensitive function of chain stiffness: for the most flexible system the chain shows *no* elongation with increasing A^* yet shows the most pronounced order–disorder transition. This behavior we are able to reconcile in terms of the development and entrapment of hairpins and shall discuss in these terms in a forthcoming Monte Carlo investigation of the system.

At large flexibilities the role of hairpins becomes crucial. Their presence permits the development of a high degree of orientational order while substantially reducing the mean-square length of the system. With decreasing temperature these high energy hairpins may be frozen out, the more readily the less flexible the system is. Hairpins are identified by $\cos \theta_{oj} \cos \theta_{oj+1} < 0$ at some point along the chain,[18] and unfortunately we have not been able to explicitly investigate the development of hairpins on the basis of the IC technique: we can only surmise their existence on the basis of the observed behavior of S and $\langle R_N^2 \rangle$. Nevertheless, we discuss the contributions arising from hairpins below.

Results determined on the basis of the IC approximation are displayed in Figure 5 from which we see that $\langle R_N^2 \rangle$ shows a discontinuous increase at the reduced isotropic–nematic transition temperature $T_{\mathrm{NI}}^* = (A_{\mathrm{NI}}^*)^{-1}$. Unlike the order parameter S, the mean-square length shows a sensitive dependence upon flexibility: as mentioned above, this we attribute to the differing orientation dependence of S and $\langle R_N^2 \rangle$.

Of particular interest is the perfectly flexible chain $\theta_{\max} = \pi$ that shows a strong first-order transition in the order parameter, while $\langle R_N^2 \rangle$ retains its random walk value regardless of the reduced temperature. It is a straightforward exercise to show that for perfectly flexible sequences of perfectly aligned rods ($S = 1$) the mean-square length is N, just as it is for the random walk result at $S = 0$. This initially surprising result is confirmed by *the Monte Carlo calculations and illustrates the subtle* role that stiffness plays in determining S and $\langle R_N^2 \rangle$. It is appropriate at this point to observe that such behavior is fully consistent with the development of hairpin states within the system, and a qualitative discussion from this point of view is given below. Although Khokhlov and Semenov[7] do not determine the order parameter for their semiflexible macromolecules, they do make passing reference to the fact that for perfectly flexible molecules the mean-square length varies insignificantly with external field, although they do report a discontinuous transition in the mean-square projection of the end-to-end distance vector on the orientation axis for such systems.

The mean-square radius of gyration $\langle S_N^2 \rangle$ shows a similar dependence to $\langle R_N^2 \rangle$ upon temperature and stiffness, as might be expected (Figure 6). Although the scattering function for such chains cannot be calculated on the basis of the IC approximation, we nevertheless anticipate the transition should be characterized by large anomalous scattering in the Guinier region with the dramatic increase in $\langle S_N^2 \rangle$ at A_{NI}^*.

The Role of Hairpins

The order parameter and length transitions may be usefully discussed in terms of hairpins, or chain reversals; indeed, de Gennes[4] has already presented a qualitative discussion in these terms. Unfortunately, as we have already explained, hairpin reversals cannot be identified on the basis of the IC analysis. Nevertheless, a qualitative discussion in terms of hairpins is possible, and their explicit contribution to the chain configurations will be presented in a subsequent MC analysis.[15] The system is regarded as a one-dimensional constrained random walk (constrained by the chain's intrinsic stiffness) linking a number, n_{H}, of hairpins. Clearly, the intrinsic stiffness of the chain implies a bending energy penalty for chain reversals executed in a small number of steps, while the external potential disfavors transverse excursions across the nematic field. Evidently there is an energy, E_{H}, associated with the formation of a hairpin, the magnitude depending upon the number of steps required to complete the reversal, the intrinsic chain flexibility, and the external potential multiplier A^*S. The probability of formation of a hairpin may be expressed in Boltzmann form and their development discussed in terms of thermal activation. Only at high temperatures (small A^*) can hairpin states be activated with significant probability and only then in systems of sufficient flexibility. With decreasing temperature (increasing A^*), the hairpins are frozen out and the system makes its transition from coil to rod and the chain length increases accordingly. The rate at which the hairpins are eliminated from the system with decreasing temperature depends, of course, upon E_{H}. For highly flexible chains the reversal can be effectively executed in two steps, incurring a very low-energy penalty: accordingly such systems show a very gradual rod–coil transition (Figure 5). Indeed, for perfectly flexible sequences chain reversals along the director carry no energy penalty and cannot be thermally eliminated. Monte Carlo simulation appears to confirm this proposal and will be reported in a subsequent publication.[15]

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(17) Note that for a uniform, spherically symmetric distribution of the end points of the vectors corresponding to a random distribution we require $Z(\cos \theta_{0j})$ = constant rather than $Z(\theta_{0j})$ = constant.
(18) The identification of $\cos \theta_{oi} \cos \theta_{oi+1} < 0$ as a hairpin does not necessarily require a sharp reversal in chain direction. Even for the stiffest chains capable of forming a hairpin (albeit in a large number of steps) there must be some point along the contour at which $\cos \theta_{oi} \cos \theta_{oi+1} < 0$.