Theory of main chain nematic polymers with spacers of varying degree of flexibility

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Theory of main chain nematic polymers with spacers of varying degree of flexibility

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Main chain liquid crystal polymers are modelled as either worms or jointed rods. In reality they are composed of mesogenic units (rods) linked by spacers with varying degrees of flexibility. We present a molecular model to describe non-homogeneous nematic polymers. The model takes account of molecular parameters, such as the lengths of the mesogenic group and the spacer units, and the interactions between them. The spacers are found to have an order differing from the mesogenic units. If the spacer is not very long and thus in effect is inflexible, one end of the spacer can retain to some extent the orientation of the other end, allowing orientational correlation between spacers mediated by the intermediate mesogenic unit. This is important in giving the chain a global rod-like behaviour as the nematic field becomes strong or the temperature low. The nematic order of the two components (mesogens and spacers), the nematic–isotropic transition as well as the latent entropy are examined. Furthermore, the anisotropic conformations of the polymers are investigated, which show either rod-like or random walk behaviour. Comparison of our results with experiment is found to be satisfactory.

1. Introduction

Most main chain liquid-crystalline polymers are composed of mesogenic groups linked by spacers with varying degrees of flexibility, such as repeated methylene, oxyethylene, or siloxane groups. The polymer is modelled either as a worm [1–4], as a rigid rod [5, 6] or as freely jointed rods. The rigid rod model is specially applicable for some lyotropic liquid crystals or biomolecules but it does not allow any flexibility of the polymer chain. However, when the chain is not completely rigid, chain flexibility in fact has a significant effect on the properties of polymers. The freely jointed rod chain treats the polymer as repeated rods, hence the polymer can be bent through the junctions. Unfortunately, it fails to deduce the transition to rod behaviour which is expected when the nematic field is strong. In a sense, the nematic worm theory has the advantage of easily describing polymers where the chain is regarded as an elastically inextensible, homogeneous chain. More recently Yurasova and Semenov [7] attacked the non-homogeneous polymer problem. They model spacers as worms, but relax the concept that the chain tangent vector is a unit vector and introduce a fixed chain length as a whole instead, in order that the standard Wiener integral can be used. However it is well-known that the relaxation of this constraint fails to give correct results even when dealing with the simple case, for example the isotropic chain [8].

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Actually, the flexible spacers are constrained by the mesogenic units to which they are linked to have some orientational order. In turn they affect the order of the mesogenic units. If the spacers are not very long and not perfectly flexible, one end of the spacer can retain to some extent the orientation of the other end, allowing the spacers to talk to each other via the intervening mesogenic unit. They thus indirectly mediate nematic interactions. It is expected that spacers have an order differing from that of the mesogenic units.

In this work the spheroidal approach [2,4] is exploited to describe the spacers, while the mesogenic groups are modelled as rods in a quadrupolar potential. The effect of the physical linkage and the van der Waals interaction between the rods and the worms is examined. The molecular parameters, such as the length of the rods and worms are also taken into account. The nematic–isotropic transition and some other statistical properties, such as the orientational order of the two components, i.e. mesogenic units and spacers, and the latent entropy are calculated as functions of the molecular parameters.

Tremendous efforts have been made to synthesize liquid crystal polymers in the last decade and many experiments have been performed to investigate the dependence of the polymer properties on their molecular parameters. Qualitative agreement of the theory is found with the experiments. Comparisons are also made with the worm-like chain model and jointed rods models including the case of freely jointed rods. One result indicates that when the characteristic length of the polymer i.e. the persistence length, is marginally greater than the monomer length, the worm-like theory is applicable with its phenomenological bend elasticity expressed by a combination of molecular parameters as shown in this paper. The approach can be extended to monomers, dimers and oligomers. We shall discuss those problems in a separate paper. Although they have the same basic chemical formulae, the monomers, dimers, oligomers, and polymers whether linear or cyclic have their own characteristics, including the nematic–isotropic transition, nematic order, and dimensions for polymers, which are all available in the literature.

2. The non-homogeneous nematic chain model

Figure 1 is a sketch of the main chain liquid crystal polymer with which we are concerned. The chain is composed in sequence of rod-like, mesogenic units, referred to as A, segments of length a each, and flexible spacers, denoted as B worm-like sections of the chain of total contour length b each; the degree of polymerization of the polymer is N. The rod-like segments A are treated in terms of a Maier–Saupe type theory [9], i.e. an orientational molecular field of quadrupolar symmetry representing both soft and steric contributions of the form $P_2(\cos\theta)$; spatially dependent interactions are not considered in this type of molecular field theory. Because there are two components A and B the soft coupling constant is diluted by a factor ρ, the volume fraction of the rod component. Assuming the two parts have the same cross section, the volume fraction is $a/(a+b)$.

The spheroidal approach [2,4] is exploited to describe the spacers, that is section B of the chain stiffness is characterized by the bend constant, ε and this yields a persistence length $l_0 = 2\varepsilon/k_B T$. Perfect flexibility (and hence loss of memory of direction when traversing B) thus corresponds to $b \gg l_0$. The B section interacts with the mesogenic units, the coupling constant being v_{ab}. In the nematic phase, the mesogenic units A impose an orientational order on the B sections, denoted S_B. S_B is not necessarily the
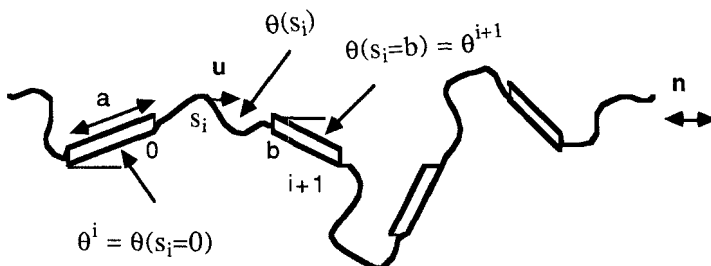
Figure 1. A sketch of a molecularly non-homogeneous nematic chain. a, b are the lengths of the A segments and B sections of the chain, respectively. $\mathbf{u}$ is the tangent vector of the chain at contour length s_i in ith monomer along the chain. $\theta(s_i)$ and θ^i are the angles which the B section at s_i and the A segment make with respect to the director $\mathbf{n}$, respectively.

same as that of the A segments, S_A. Usually $S_B < S_A$, i.e. the flexible part is less ordered than the mesogenic part. Both are ensemble averaged over all the segments, i.e.

$$S_A = \frac{1}{N} \left\langle \sum_{i=1}^{N} P_2(\mathbf{u}^i \cdot \mathbf{n}) \right\rangle_{\text{all A segments}},$$

$$S_B = \frac{1}{N} \left\langle \sum_{i=1}^{N} P_2(\mathbf{u}(s_i) \cdot \mathbf{n}) \right\rangle_{\text{all B sections}},$$

$$\tag{1}$$

where $P_2(x)$ is the second Legendre polynomial, $\mathbf{u}$ is either the tangent vector $\mathbf{u}(s_i)$ describing the ith B chain at contour length s_i or the tangent vector $\mathbf{u}^i$ that describes the direction of the rod part (A) of the ith monomer. $\mathbf{n}$ is the preferred direction, i.e. the director.

The order parameter of the system as a whole S is expressed by the volume weighted mean of orders of the two components

$$S = \rho S_A + (1-\rho)S_B. \tag{2}$$

The order parameter measured by birefringence will be weighted not only by volume fraction but also by the relative dielectric anisotropy. By selective deuteration, NMR can measure S_A and S_B separately; in fact we can measure S_B as a function of distance along the spacer. Our model, since it describes the worm-like segments, contains information about their order along their length s, that is $S_B(s)$ but we do not present these data here.

Generally, there are three interactions in the system: the A–A, B–B and A–B interactions, represented by coupling constants per unit arc length v_{aa}, v_{bb} and $v_{ab}(v_{ab} = v_{ba})$. The hamiltonian of the ith monomer consisting of an A segment linked with a B section, H^i, is

$$H^i = -[v_{aa}\rho S_A + v_{ab}(1-\rho)S_B]aP_2(\mathbf{u}^i \cdot \mathbf{n})$$

$$+ \int_0^b \left\{ -[v_{ab}\rho S_A + v_{bb}(1-\rho)S_B]P_2(\mathbf{u}(s_i) \cdot \mathbf{n}) + \frac{\varepsilon}{2}\left(\frac{d\mathbf{u}}{ds_i}\right)^2 \right\} ds_i$$

$$\equiv -W_A aP_2(\mathbf{u}^i \cdot \mathbf{n}) + \int \left\{ -W_B P_2(\mathbf{u} \cdot \mathbf{n}) + \frac{\varepsilon}{2}\left(\frac{d\mathbf{u}}{ds_i}\right)^2 \right\} ds_i,$$

$$\tag{3}$$

where the couplings W_A and W_B are

$$W_A = v_{aa}\rho S_A + v_{ab}(1-\rho)S_B,$$
$$W_B = v_{ab}\rho S_A + v_{bb}(1-\rho)S_B. \tag{4}$$

The subscripts A and B denote the A and B segments, respectively. Because of the lengths a and b in equations (3), when H^i is expressed as an energy per volume, then the factors of ρ and $(1-\rho)$ will effectively become ρ^2, $\rho(1-\rho)$ and $(1-\rho)^2$ in the usual expected way. The total hamiltonian H is the summation over all of the N monomers

$$H = \sum_{i=1}^{N} H^i. \tag{5}$$

So far this theory would be appropriate for a mixture of unconnected A and B segments. We connect them together, insisting that spacer and rod, at their junction have the same orientation. This represents an additional effective orientational A–B coupling and indirectly A–A and B–B coupling (mediated by the intervening species). The partition function Z of the polymer chain results from summing over all angles θ^i for the rod (A) segments and over all choices of the shapes of chains $\mathbf{u}(s_i)$ for the B sections

$$Z = \int \prod_{i=1}^{N} d(\cos \theta^i) \int \sum_{i=1}^{N} D\{\mathbf{u}(s_i)\} \exp\left[\sum_{i=1}^{N} \beta a W_A P_2(\cos \theta^i)\right]$$

$$\times \exp\left\{\sum_{i=1}^{N} \int_0^b \left[\beta W_B P_2(\cos \theta(s_i)) - \frac{\beta\varepsilon}{2}\left(\frac{d\mathbf{u}}{ds_i}\right)^2\right] ds_i\right\}$$

$$\times \prod_{i=1}^{N} \delta(\theta^i - \theta(s_i=0)) \prod_{i=1}^{N-1} \delta(\theta^{i+1} - \theta(s_i=b)), \tag{6}$$

where the Dirac delta functions, δ, ensure that the ends of spacers, B, have the same orientation as the successive A rods to which they are attached (see figure 1) and β is $1/k_B T$. In terms of the spheroidal model of worm-like chains [2, 4], the part of Z concerned with each B section can be expressed by the spheroidal wavefunctions. It is simply the conditional probability (Green function or propagator) that a chain starting with angle $\theta(s_i=0)=\theta_0$ from one rod, ends with $\theta(s_i=b)=\theta_b$ at the next:

$$G(\theta_b, \theta_0; b) = \sum Sp_n(\theta_0)Sp_n(\theta_b)\exp(-\lambda_n b/l_0),$$

where λ_n and Sp_n are the nth eigenvalue and eigenfunction of the spheroidal wave equation of zeroth-rank. For simplicity we assume $Sp_n(\theta)$ is normalized to unity. Performing the sums over rod directions (the δ-functions simply set them equal to the directions of the relevant chain ends), the partition function becomes

$$Z = \int \prod_{i=1}^{N} \exp\left[\beta a W_A P_2(z_0^i)\right] \prod_{i=1}^{N-1} (z_b^i - z_0^{i+1})$$

$$\times \prod_{i=1}^{N} [Sp_0(z_0^i)Sp_0(z_b^i)\exp(-\lambda_0 b/l_0)\,d(z_0^i)\,d(z_b^i)]. \tag{7}$$

We have changed to the more natural variable, $z = \cos\theta$, and taken only the ground state $n = 0$ in G. With this restriction the partition function Z is simply given by

$$Z = \exp(-\lambda_0 Nb/l_0)\left\{\int \exp[\beta a W_A P_2(z)][Sp_0(z)]^2\, dz\right\}^{N-1}$$

$$\times \left\{\int Sp_0(z_N)\, dz_N\right\}\left\{\int \exp[\beta a W_A P_2(z_1)]Sp_0(z_1)\, dz_1\right\}. \tag{8}$$

The next state to be involved is, for symmetry reasons, $n = 2$. We discuss this in detail in an appendix but at this stage note that we require $\exp[-(\lambda_2 - \lambda_0)b/l_0]$ to be small. In the nematic state $\lambda_2 - \lambda_0$ rapidly becomes large and this requirement becomes more easily satisfied. When the degree of polymerization N is high, we neglect the terms without the N factor in $\log(Z)$ and hence Z becomes

$$Z \cong \exp(-\lambda_0 Nb/l_0)\left\{\int \exp[\beta a W_A P_2(z)][Sp_0(z)]^2\, dz\right\}^N. \tag{9}$$

The total free energy per polymer has the form

$$F = -k_B T \ln Z - \tfrac{1}{2}\langle U\rangle, \tag{10}$$

where the first part arises from the partition function and the second term is from mean field theory to avoid double counting pair interactions. Putting Z and U into equation (10) yields

$$F/(Nk_B T) = \frac{\beta}{2}(a W_A S_A + b W_B S_B) + \lambda_0 b/l_0$$

$$- \ln\left\{\int \exp[\beta a W_A P_2(z)][Sp_0(z)]^2\, dz\right\}. \tag{11}$$

The second and third terms are familiar as the mean field free energy of a worm chain of length Nb. The first term is the usual Maier–Saupe molecular field term for an isolated rod. The last term would simply be that of Maier–Saupe if the spacers were isotropic (the function $Sp_0(z) = 1$). The deviation from the simple rod form comes from additional orientational effects in the worm chain tied to each end of a rod segment—the two factors of $Sp_0(z)$ included in the rod partition integral. It is the term that makes the problem differ from simply that of rods mixed with nematogenic worm chains.

3. Orientational order

We denote the following integrals as matrix elements for simplicity

$$G_{m,n} = \int_{-1}^{1} \exp[\beta a W_A P_2(z)]Sp_m(z)Sp_n(z)\, dz, \tag{12a}$$

$$G_{m,n}^{[1]} = \int_{-1}^{1} P_1(z)\exp[\beta a W_A P_2(z)]Sp_m(z)Sp_n(z)\, dz, \tag{12b}$$

$$G_{m,n}^{[2]} = \int_{-1}^{1} P_2(z)\exp[\beta a W_A P_2(z)]Sp_m(z)Sp_n(z)\, dz. \tag{12c}$$

Minimizing the free energy in equation (11) with respect to S_A and S_B yields the order parameters of both A segments and B sections. The order parameter of the A segments is then given by

$$S_A = \frac{\int_{-1}^{1} \exp\left[\beta a W_A P_2(z)\right][S p_0(z)]^2 P_2(z)\, dz}{\int_{-1}^{1} \exp\left[\beta a W_A P_2(z)\right][S p_0(z)]^2\, dz},$$

$$= G_{00}^{[2]}/G_{00} \qquad (13)$$

The discussion of the new rod term in equation (11) for F is underlined by this result: when averaging $P_2(z)$ the probability $\exp(\beta a W_A P_2(z))$ is enhanced by the orientational tendency of the worms to which the rod is attached. The order of the B sections is then

$$S_B = \frac{3}{2} \frac{\partial \lambda_0}{\partial \Delta^2} - \frac{3 l_0}{b} \frac{\int \exp\left[\beta a W_A P_2(z)\right] S p_0(z) \dfrac{\partial S p_0(z)}{\partial \Delta^2}\, dz}{\int \exp\left[\beta a W_A P_2(z)\right][S p_0(z)]^2 dz}. \qquad (14)$$

The coupling constant Δ^2 is an important parameter in the spheroidal approach, $\Delta^2 = -3\beta^2 \varepsilon W_B$. It is what determines the functions $S p_n(z)$ and the λ_n are purely a function of Δ^2. Actually we transformed from the S to the W variables in the calculation. The Pauli trick [6] gives the derivatives of λ_0 and $S p_0$ with respect to Δ^2 in terms of the matrix elements. Consequently, S_B is

$$S_B = (P_2)_{00} + \frac{2 l_0}{b} \sum_{n=2}^{\text{even}} \frac{(P_2)_{0n}}{\lambda_n - \lambda_0} \frac{G_{0n}}{G_{00}}, \qquad (15)$$

where $(P_2)_{0n} = \int S p_0(z) P_2(z) S p_n(z)\, dz$, and where the second term arises from the ends of spacers connected with rigid rods. When the chain is long enough compared with the persistence length, l_0, the second part is small and may be neglected [4]. For the underlying polymers the second part makes an important contribution to the order parameter, which is attributed to the fact that the rods impose the orientational order on conjugated B sections, and the B section is not very long. Substituting S_A and S_B into equation (2) gives the resultant order parameter of the system. The spheroidal wavefunctions are expanded in a basis set of Legendre polynomials [4] in our numerical calculation. Figure 2 shows the dependence of the orientational order of the mesogen, the spacer parts and of the whole polymer, S_A, S_B and S. S_A has a typically Maier–Saupe-like temperature dependence. S_B is a distinctly different function of temperature varying enormously with the polymer parameters. In the temperature region where S_A undergoes its transition the B sections are actually in the paranematic state under the influence of the nematic field of the A segments. S_B is therefore small. As the temperature decreases the B sections order and thus S_B becomes greater; S_B is in general less than the order of the mesogenic units, A.

4. Nematic–isotropic phase transition

When the nematic–isotropic transition occurs the free energy of the phases is equal

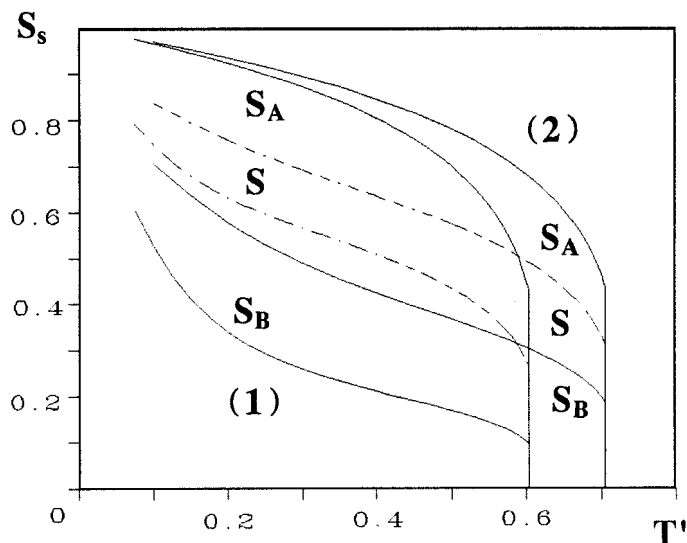$$\Delta F/(N k_B T) = \frac{\beta}{2}(a S_A W_A + b S_B W_B) + \lambda_0 b/l_0 - \ln(G_{00}) = 0. \qquad (16)$$

Figure 2. Nematic order of the whole system and its two individual parts, i.e. mesogen and spacer, as a function of T', the temperature reduced by the nematic–isotropic transition temperature of the Maier–Saupe model for pure rods of length a. The two families of curves corresponding to $a:b:l_0 = 2:2:1$ (1) and $1:1:1$ (2). The interaction constants $v_{aa}:v_{ab}:v_{bb}$ are $1:0.5:0.2$.

We normalize the temperature by the Maier–Saupe transition temperature for pure rigid rods of length, a, $T_0 = 0.2202av_{aa}/k_B$. An advantage of doing so is that T_0 may be available in the literature. For given molecular parameters, such as the interaction ratio, $v_{aa}:v_{ab}:v_{bb}$, the length ratio $a:b:l_0$, and hence the volume fraction ρ, the nematic–isotropic transition temperature of the liquid-crystalline polymers is plotted against the molecular parameters and will be discussed later. The temperature scale is relative to the Maier–Saupe value of the nematic–isotropic transition temperature, T_0. We shall adopt this reduction of temperature in all that follows, for instance $T_{red} = T_{NI}/T_0$ is the nematic–isotropic temperature reduced by the Maier–Saupe value for rods of length a.

In this calculation, the coupling constants W_A and W_B or Δ^2 are expressed in terms of the molecular parameters as

$$\beta_a W_A = \frac{1}{0.2202} \frac{T_0}{T} \left[\rho S_A + (1-\rho)\frac{v_{ab}}{v_{aa}} S_B \right] \tag{17}$$

and

$$\Delta^2 = -3\beta^2 \varepsilon W_B = -\frac{3}{2}\frac{1}{0.2202}\frac{l_0}{b}\frac{T_0}{T}\left[(1-\rho)\frac{v_{ab}}{v_{aa}}S_A + \frac{(1-\rho)^2}{\rho} - \frac{v_{bb}}{v_{aa}}S_B\right]. \tag{18}$$

5. Latent entropy

The entropy of a chain is given by [6]

$$S_N = k_B \ln Z - k_B \beta \frac{\partial}{\partial \beta} \ln Z. \tag{19}$$

Putting Z of equation (9) into equation (19) we obtain the entropy S_N in the nematic state as

$$S_N/(Nk_B) = -\lambda_0 \frac{b}{l_0} + \ln(G_{00}) - \beta \left[\frac{\partial}{\partial\beta} \ln(G_{00}) - \frac{b}{l_0} \frac{\partial\lambda_0}{\partial\beta} \right]. \qquad (20)$$

The derivatives $\partial/\partial\beta$ in the last term are complicated but can be simplified with the aid of expressions (13) and (15). Consequently, the latent entropy per monomer at the nematic–isotropic transition, ΔS_N, is

$$\Delta S_N/k_B = \frac{\beta}{2}(bW_B S_B + aW_A S_A)$$

$$= \frac{\beta}{2}(a+b)[v_{bb}(1-\rho)^2 S_B^2 + 2v_{ab}\rho(1-\rho)S_A S_B + v_{aa}\rho^2 S_A^2]. \qquad (21\,a)$$

If we take into account the temperature dependence of $l_0 = 2\beta\varepsilon$, the latent entropy becomes

$$\Delta S_N/k_B = \frac{\beta}{2}(2bW_B S_B + aW_A S_A). \qquad (21\,b)$$

It is obviously the additional temperature dependence of the persistence length that makes an extra contribution to the latent entropy, the factor of 2 in the first term. This change improves agreement with experiment, but the prediction is still low.

6. Dimensions

The end-to-end vector of the polymer is

$$\mathbf{R}(L) - \mathbf{R}(0) = \int_0^L ds\,\mathbf{u}(s) = \sum_{i=1}^N \left[a\mathbf{u}^A(s^i) + \int_0^b ds\,\mathbf{u}^B(s_i) \right]. \qquad (22)$$

Then the two principal values of mean square end-to-end tensor are given in terms of the orientational correlation functions as

$$\langle R_z^2 \rangle = a^2 \sum_i \sum_j \langle \cos\theta_i^A \cos\theta_j^A \rangle + \sum_i \sum_j \int\int_0^b ds_i ds_j \langle \cos\theta^B(s_i) \cos\theta^B(s_j) \rangle$$

$$+ 2a \sum_i \sum_j \langle \cos\theta_i^A \int_0^b ds_j \cos\theta^B(s_j) \rangle, \qquad (23\,a)$$

$$\langle \mathbf{R}_p^2 \rangle = a^2 \sum_i \sum_j \langle P_1^1(\theta_i^A) P_1^{-1}(\theta_j^A) \exp[-i(\varphi_i^A - \varphi_j^A)] \rangle$$

$$+ \sum_i \sum_j \int\int_0^b ds_i ds_j \langle P_1^1(\theta^B(s_i)) P_1^{-1}(\theta^B(s_j)) \exp\{-i[\varphi^B(s_i) - \varphi^B(s_j)]\} \rangle$$

$$+ 2a \sum_i \sum_j \langle P_1^1(\theta_i^A) \int_0^b ds\, P_1^{-1}(\theta^B(s_j)) \exp\{-i[\varphi_i^A - \varphi^B(s_j)]\} \rangle, \qquad (23\,b)$$

where P_1^{-1} and P_1^{-1} are associated Legendre polynomials. After taking all of the orientational correlation functions the polymer mean square dimensions parallel to the director is

$$\langle R_z^2 \rangle = Na^2 \left\{ \frac{2}{3}\frac{G_{00}^{[2]}}{G_{00}} + \frac{1}{3} + 2\exp\left[-\lambda_1-\lambda_0)b/l_0\right]\left[\frac{G_{01}^{[1]}}{G_{00}}\right]^2\left[\frac{1}{1-x}-\frac{1}{N}\frac{1-x^N}{(1-x)^2}\right]\right\}$$

$$+ N[(P_1)_{01}]^2\left\{\frac{2bl_0}{(\lambda_1-\lambda_0)}\left[1-\frac{1-\exp\left[-(\lambda_1-\lambda_0)b/l_0\right]}{b/l_0(\lambda_1-\lambda_0)}\right]\right.$$

$$+ 2\left[\frac{1-\exp\left[-(\lambda_1-\lambda_0)b/l_0\right]}{(\lambda_1-\lambda_0)/l_0}\right]^2\frac{G_{11}}{G_{00}}\left[\frac{1}{1-x}-\frac{1}{N}\frac{1-x^N}{(1-x)^2}\right]\right\}$$

$$+ 2a(2N+1)\frac{1-\exp\left[-(\lambda_1-\lambda_0)b/l_0\right]}{(\lambda_1-\lambda_0)/l_0}(P_1)_{01}$$

$$\times \frac{G_{01}^{[1]}}{G_{00}}\left[\frac{1}{1-x}-\frac{2-x^N-x^{N+1}}{(2N+1)(1-x)^2}\right], \tag{24}$$

where $(P_1)_{01} = \int Sp_0(z)P_1(z)Sp_1(z)\,dz$ and

$$x = \frac{G_{11}}{G_{00}}\exp\left[-(\lambda_1-\lambda_0)b/l_0\right], \tag{25}$$

whether or not the chain takes a rod-like or a random walk depends on x.

The dimension along the director, $\langle R_z^2 \rangle$, is depicted in figure 3 (*a*) as a function of temperature relative to nematic–isotropic transition temperature of the polymer. The curves in figure 3 are given for several values of the spacer length reduced by the persistence length, $b/l_0 = 0.5$, 1, and 2. It is shown that the dimension depends critically on the ratio b/l_0. If the chain length is either long enough or very flexible the conformation of the polymer is basically a random walk. When the temperature is low the conformation of the polymer as a whole makes a transition to being rod-like, but if b/l_0 is smaller, the polymer behaves in rather a rod-like manner. For comparison the curves of freely jointed rods and the nematic worm chain are also drawn in figure 3 (*a*). It is seen that the freely jointed rod model never becomes rod-like, while the worm chain model is somewhat like the results here.

The strong nematic limit, i.e. $\Delta^2 \to -\infty$, sees $x \to 1$. In equation (25) we have $\lambda_1 \to \lambda_0$ in this limit and hence the exponential factor $\to 1$. Likewise, the factors G_{00} and G_{11} depend on $(Sp_0)^2$ and $(Sp_1)^2$ and in this limit these are sharply peaked around $\theta = 0, \pi$ and become identical. In the limit $x \to 1$ the factors $[1/(1-x)+\ldots]$ in equation (24) converge to

$$N\left[\frac{1}{1-x}-\frac{1}{N}\frac{1-x^N}{(1-x)^2}\right]_{x\to 1} \to \frac{N}{2}(N-1) \tag{26}$$
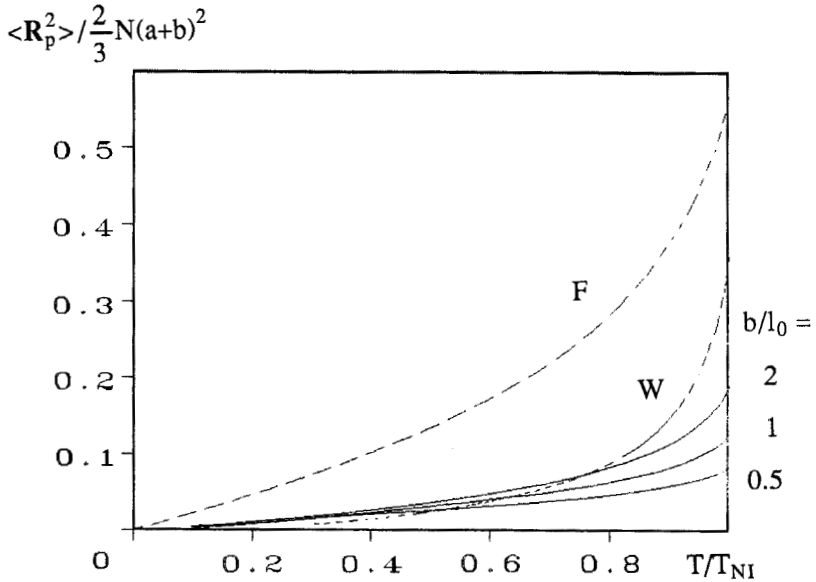
and

$$(2N+1)\left[\frac{1}{1-x}-\frac{2-x^N-x^{N+1}}{(2N+1)(1-x)^2}\right]_{x\to 1} \to N^2 \tag{27}$$

thus the mean square dimension parallel to the director becomes $N^2(a+b)^2$ which is expected from a perfectly ordered nematic polymer.

$\langle R_z^2 \rangle / N^2(a+b)^2$

(a)

$\langle \mathbf{R}_p^2 \rangle / \frac{2}{3} N(a+b)^2$
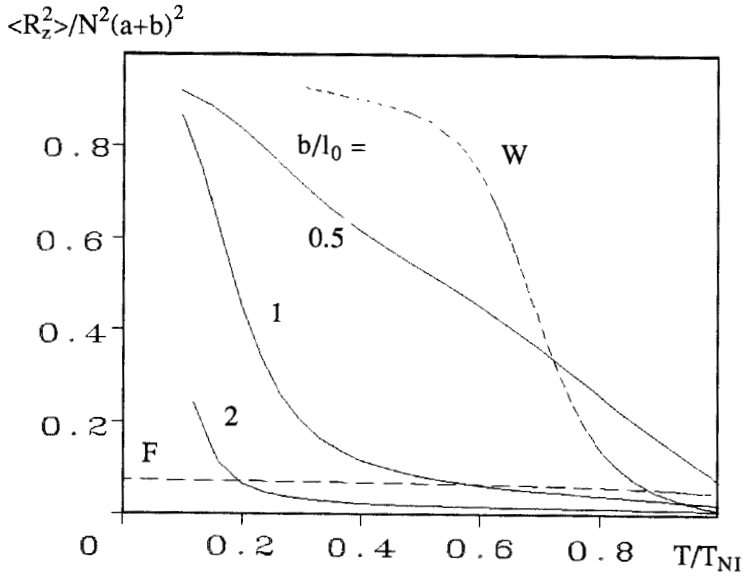
(b)

Figure 3.   The mean square dimensions parallel to the director, $\langle R_z^2 \rangle / N^2(a+b)^2$ (a), and in the
plane perpendicular to the director $\langle \mathbf{R}_p^2 \rangle / 2N(a+b)^2/3$ (b), as functions of temperature
reduced by the nematic–isotropic transition temperature of the polymers. The curves
correspond to $b/l_0 = 0.5$, 1, 2, respectively. The dashed lines marked by F and W are drawn
for the freely jointed rods model and worm model, respectively.

In the isotropic state, $x = \exp(-2b/l_0)$, equation (24) is reduced to, after substituting $\lambda_n = n(n+1)$ and $Sp_n = P_n$, the values at $\Delta^2 = 0$,

$$\langle R_z^2 \rangle = \tfrac{1}{3}Na^2 + \tfrac{1}{3}Nbl_0 \left(1 - \frac{1}{2b/l_0} + \frac{\exp(-2b/l_0)}{2b/l_0} \right) + \tfrac{2}{3}a^2(N-1)\exp(-2b/l_0)$$

$$+ \frac{l_0^2}{6}[N - 1 - \exp(-2b/l_0)] + \tfrac{1}{3}al_0[2N - 1 - 2\exp(-2b/l_0)], \qquad (28)$$

where the first term is attributed to the A rods in a random walk, the second to the B worm spacers. The remaining three terms arise from requiring that rod and spacer have the same orientation at their junction. The approximations of $b/l_0 \gg 1$ and $N \gg 1$ further reduce equation (28) to

$$\langle R_z^2 \rangle = \tfrac{1}{3}N[a(a + 2l_0) + bl_0]. \qquad (29)$$

We notice that the step length for an A segment is no longer purely that of an individual rod because of the physical linkage between rods and spacers in a non-homogenous polymer.

The mean square end-to-end distance $\langle \mathbf{R}_p^2 \rangle$ in the plane perpendicular to the director has a form analogous to that of $\langle R_z^2 \rangle$, but with P_1^1 instead of z (i.e. P_1), Sp_1^1 instead of Sp_1 and λ_1^1 instead of λ_1, where Sp_1^1 and λ_1^1 are the eigenfunction and eigenvalue of the first rank spheroidal wavefunction. The dependence of $\langle \mathbf{R}_p^2 \rangle$ as a function of the reduced temperature is plotted in figure 3 (b). Because the dimension perpendicular to the director, i.e. $\langle \mathbf{R}_p^2 \rangle$, is basically a random walk figure 3 (b) is plotted so that the vertical scale is relative to the random walk value for chains with step length $(a+b)$ instead. This is in contrast to the choice of the perfectly ordered state in the case of $\langle R_z^2 \rangle$.

If the persistence length of the polymer is greater than the monomer length the nematic worm model [2,4] is applicable. By comparison with equation (29) the effective bend elasticity can be extracted and is predicted to be

$$\varepsilon_{\text{eff}} = (1 + \rho)\varepsilon + \rho^2(a + b)/2\beta \qquad (30)$$

which builds a bridge between the molecularly non-homogenous model and the worm chain model. As the spacer becomes very short ground state dominance is no longer valid (i.e. consideration of only the $n = 0$ state). An extreme, the elastic jointed rods case, is addressed elsewhere [10]. If the mesogens become short enough and meanwhile the flexibility of the spacers decreases, the other extreme, it reduces to the worm chain.

7. Results and discussion

The nematic–isotropic transition, including aspects such as the transition temperature, order parameters and latent entropy, depends on polymer parameters, such as the lengths a, b, l_0 and the interactions v_{aa}, v_{ab} and v_{bb}; these are shown in figures 4–8. One of our important results shows the effect of the length of flexible spacer, b, on the transition. The reduced transition temperature T_{red} decreases significantly when b increases while the latent entropy increases, as shown in figure 4. It is confirmed by many experiments [11–13] in which the transition temperature decreases substantially as the number of carbon atoms in the spacers increases. Such transitions also show the odd–even effect [11], however it will not be dealt with in this paper. This model could accommodate the odd–even effect by fixing for odd/even spacers a variable offset angle

between the rod and the attached worm spacer to replace the single constraint on the angles in equation (6).

It has been found from experiment that most polymers with short spacers are neither fusible nor show a nematic phase until decomposition [11]. In contrast, low molecular mass liquid crystals composed of the same mesogenic units exhibit a nematic phase, even though their flexible chains are short. This fact confirms our expectation, see figure 4, where the reduced nematic–isotropic transition temperature is much greater than unity when b is small and it may be far beyond the temperature of experiments under which the polymers may still be in the condensed phase. The limit $b \to 0$ (at fixed a) forces the rods to act effectively as one single long rod (their hinges having become stiff). T_{red} in figure 4 is the transition temperature relative to that of a rod segment unconnected to others, and hence it must increase ultimately to $\sim N$ as $b \to 0$.

Van Luyen and Stzelecki [14] attempted to alter the size of the rod while keeping constant the number of methylene units, all having $n = 9$, of several polyesters. They found that the value of the nematic–isotropic transition temperature increases with the length of rods, the lengths being 13, 19, 25 Å, which correspond to 200, 305, 350°C, respectively. This trend is also seen in the curve of T_{red} in figure 5. The limit $a/b \to 0$ at fixed b, i.e. without rigid rods, actually corresponds to the worm chain limit. Substituting the relations, such as $v_{aa} : v_{bb} = 1 : 0.2$ and $a = 4l_0 = 4(2\beta\varepsilon)$, and the worm chain result $k_B T_{NI}/\sqrt{(v_{bb}\varepsilon)} = 0.388$ [4] we estimate T_{red} in the plot in figure 5 to be about 0.017, just as observed from the curve in this figure. The other limit, $a \to \infty$ at fixed b, shows an increase in T_{red} since this is relative now to the transition temperature of unconnected rods of length $a = 4$.

Ober et al. summarized the experimental data in their review paper [15], which includes the effect of the flexibility of the spacers on T_{NI}. The polymers, such as
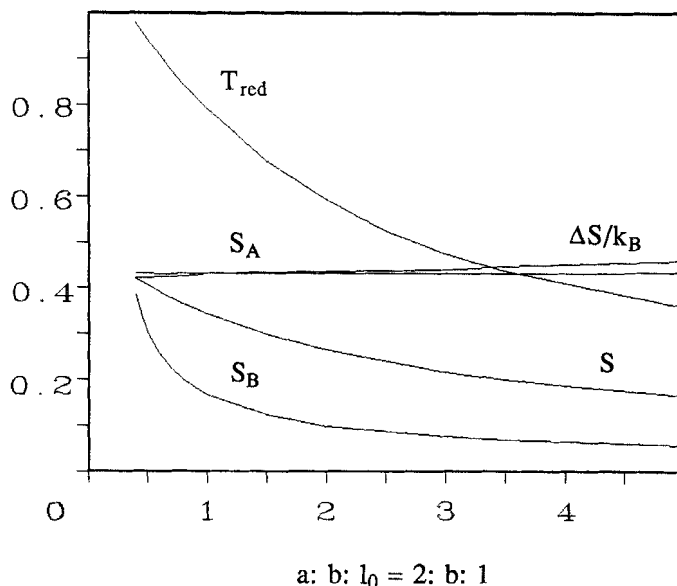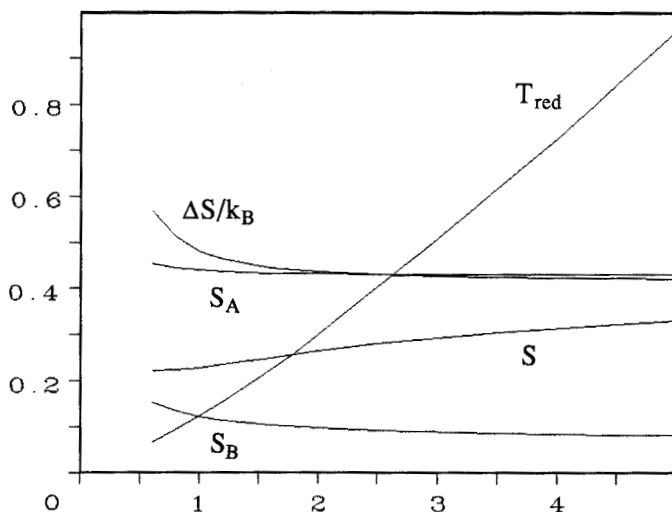
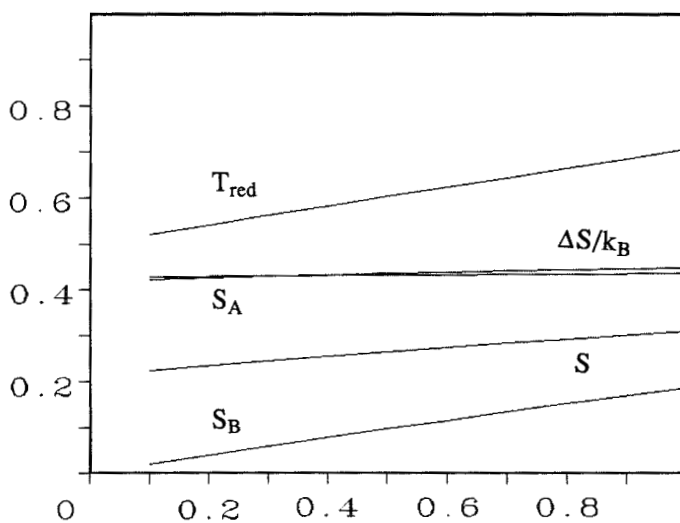a: b: l_0 = 2: b: 1

Figure 4. Depencence on spacer length b of the nematic–isotropic transition temperature T_{red}, relative to the Maier–Saupe transition temperature for pure rods of length a, order parameters, and latent entropy.
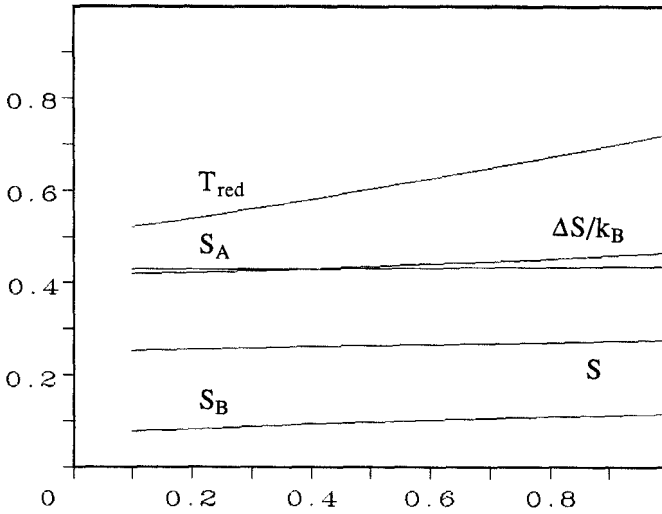
a: b: l_0 = a: 2: 1

Figure 5. Dependence on the mesogen length a of the nematic–isotropic transition tempera-
ture, relative to the Maier–Saupe transition temperature for pure rods with length $a=4$,
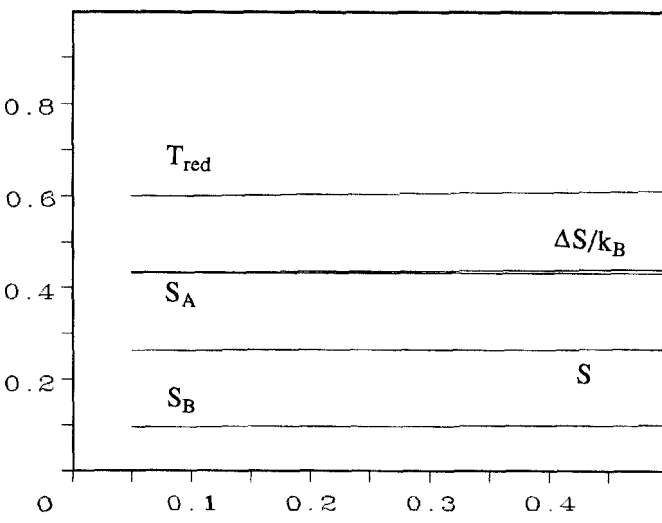order parameters, and latent entropy.

a: b: l_0 = 2: 2: l_0

Figure 6. Dependence on the persistence length l_0 of the nematic–isotropic transition
temperature, relative to that of the Maier–Saupe theory for pure rods of length a, order
parameters, and latent entropy.

$$v_{aa} : v_{ab} : v_{bb} = 1 : v_{ab} : 0.2$$

Figure 7. Dependence on the interaction ratio v_{ab}/v_{aa} of the nematic–isotropic transition temperature, relative to that of the Maier–Saupe model for pure rods of length a, order parameters, and latent entropy.

$$v_{aa} : v_{ab} : v_{bb} = 1 : 0.5 : v_{bb}$$

Figure 8. Dependence on the interaction ratio v_{bb}/v_{aa} of the nematic–isotropic transition temperature, relative to that of the Maier–Saupe theory for pure rods of length a, order parameters, and latent entropy.

polymethylene, polyoxyethylene and polysiloxane were addressed. Polysiloxane is more flexible than the other two as suggested, for example, by Ober *et al.* [15], accordingly the polymer exhibits a lower transition temperature, which is experimentally observed as well by Ober *et al.* [15]; such phenomenon is predicted in figure 6. A smaller persistence length l_0 corresponds to a more flexible chain. The polymers become Maier–Saupe systems as $l_0/b \to 0$. In this limit the spacers are completely flexible and the rods effectively independent of each other. Extrapolating the curve of T_{red} versus l_0 in figure 6 to the limit $l_0 = 0$ we obtain the reduced transition temperature $T_{red} = 0.5$, a value appropriate for a dilute rod system with $\rho = 0.5$ (due to $a = b$ in this case) which behaves like an effective interaction with respect to the unconnected case by which the temperature is being reduced. In the limit the perfect flexible spacers completely decouple the rigid rods.

Although the predicted latent entropy is qualitatively in agreement with experiment [11], it is smaller in value by a factor of about 2. The discrepancy may be due in part to the equal cross-section approximation. The rigid rods usually have a greater contribution to the latent entropy according to equation (21) and the cross-section of rods is usually greater than that of spacers. Therefore equation (21) may underestimate the latent entropy.

The fact that the transition temperature of the polymers shows the same tendency as their low molecular mass liquid crystal counterparts with the mesogens as cores, see also [15], is predicted in our theory in the manner of the normalization factor in T_{NI}. By definition the reduced temperature T_{NI} is inversely proportional to v_{aa}, so higher v_{aa} gives a larger transition temperature.

Figures 7 and 8 show the effect of the interactions v_{ab} and v_{bb} on the nematic–isotropic transition temperature, which is approximately proportional to the ratio v_{ab}/v_{aa}. It is, however, rather difficult to investigate the effect of v_{ab}, which depends critically on the chemical structure and the configuration of the polymer molecules. Meanwhile the ratio v_{bb}/v_{aa} does not visibly affect the properties of the polymer. The results indicate that the order parameter of the mesogenic unit at the nematic–isotropic transition essentially does not vary, remaining at about 0·434 while there is significant variation in that of the flexible spacer.

One extreme case, where the worm spacer flexibility decreases and the sections of the rigid rod become short, is the nematic worm chain limit. The other limit is where the worm spacer becomes so short, and hence effectively the spacer as a whole is of limited flexibility, so that successive rods have strong angular correlations induced between them. This case corresponds to the model of elastically jointed nematic rods, also treated elsewhere. Experiments are being carried out on polymers with deuteriated spacers, and/or deuteriated mesogenic groups. Neutron experiments will yield conformational information while NMR will yield order parameters, their precise values depending on detailed geometrical constraints. We have predicted the averaged values. The results of such experiments may be used to test the theory.

Yurasova and Semenov [7] are specially interested in very long spacers. But it is actually not the case of real systems in which the persistence length is about the order of the spacer length. As is well-known, the relaxation of the condition of tangent of chains being a unit vector fails to deal with chains when they are not very long, so we expect a less reliable result from their calculation for short spacers. Also they produce fewer results to compare either with ours or with experiment. Some results seem strange, for instance, they do not reproduce the Maier–Saupe expectation when rods are very long, such as the order parameter at the nematic–isotropic transition.

Appendix

Only the first two states in Z, i.e. the ground state and the first excited state have been taken into account in the model so far. The reason for the approximation is based on the evidence that the eigenvalues, which appear in the exponential in the propagator G, coalesce in pairs as Δ^2 becomes large. For instance λ_1 and λ_0 come together, as do the next eigenvalues λ_2 and λ_3 while at the same time becoming distant from λ_0 and λ_1, thus giving these terms exponentially smaller weight. Inserting the second two excited states into the partition function yields

$$Z = \int \ldots \prod_{i=1}^{N} \{\exp\left[\beta a W_A P_2(z_0^i)\right][Sp_0(z_0^i)Sp_0(z_b^i)\exp\left(-\lambda_0 b/l_0\right) + Sp_1(z_0^i)Sp_1(z_b^i)$$

$$\times \exp\left(-\lambda_1 b/l_0\right) + Sp_2(z_0^i)Sp_2(z_b^i)\exp\left(-\lambda_2 b/l_0\right)]\, d(z_0^i)\, d(z_b^i)\} \prod_{i=1}^{N-1}(z_b^i - z_0^{i+1}). \quad (A\,1)$$

The terms in Sp_1 give zero on symmetry grounds (they are dipolar in character and vanish in the quadrupolar medium). After integrating Z reduces to

$$Z = \exp\left(-\lambda_0 N b/l_0\right)(G_{00})^N \left\{1 + {}^N C_1 \exp\left[-(\lambda_2 - \lambda_0)b/l_0\right]\left(\frac{G_{02}}{G_{00}}\right)^2 \right.$$

$$\left. + {}^N C_2 \exp\left[-2(\lambda_2 - \lambda_0)b/l_0\right]\left(\frac{G_{02}}{G_{00}}\right)^4 \left[1 + \frac{2}{N-2}\frac{G_{22}G_{00}}{(G_{02})^2}\right] + \ldots\right\}. \quad (A\,2)$$

The ratio of the i-th and $(i-1)$th terms is approximately

$$\frac{N-i}{i}\exp\left[-(\lambda_2 - \lambda_0)b/l_0\right]\left(\frac{G_{02}}{G_{00}}\right)^2. \quad (A\,3)$$

The formulae from equation (9) are expected to be good provided the following condition is satisfied, i.e. the immediate next term in Z which is neglected in equation (9) must be less than unity

$$N \exp\left[-(\lambda_2 - \lambda_0)b/l_0\right]\left(\frac{G_{02}}{G_{00}}\right)^2 \ll 1 \quad (A\,4)$$

or

$$b/l_0 > \frac{1}{\lambda_2 - \lambda_0}\ln\left[N\left(\frac{G_{02}}{G_{00}}\right)^2\right]. \quad (A\,5)$$

The other potentially important term is the middle one in equation (A 2) which is approximately

$$N_{C_{N/2}}\exp\left[-\frac{N}{2}(\lambda_2 - \lambda_0)b/l_0\right]\left(\frac{G_{02}}{G_{00}}\right)^N. \quad (A\,6)$$

The combinatorial factor in this expression is 2^N according to the Stirling approximation to $N!$. Comparing with the first term in equation (A 2), this is unity, yields the inequality

$$b/l_0 > \frac{1}{\lambda_2 - \lambda_0}\ln\left[4\left(\frac{G_{02}}{G_{00}}\right)^2\right]. \quad (A\,7)$$

which is less stringent on b/l_0 that is the inequality in equation (A 5). The other terms are, as sketched in equation (A 2), even more negligible.

The matrix element ratio (G_{02}/G_{00}) is usually much less than unity, and the eigenvalue difference $(\lambda_2 - \lambda_0)$ is much greater than six, the non-nematic field value. Assuming the worst case where the matrix element ratio is unity and the eigenvalue difference is six (actually they never appear together), and taking typical values $N = 20$, 100 or 400 yields the condition on spacer length: $b/l_0 > 0.499, 0.768$ or 0.998. The results do not change very much as N becomes even larger because of the logarithm in equation (A 5). The numerics confirm that for typical values $a:b:l_0 = 2:2:1$, and $v_{aa}:v_{ab}:v_{bb} = 1:0.5:0.2$, the left hand side of equation (A 5) is always below 8×10^{-4} N, and further is less at the nematic–isotropic transition where $\Delta^2 = -1.7$. It demonstrates that equation (A 5) holds for a wide range of chain length. Above values for b/l_0 are actually an underestimate.

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