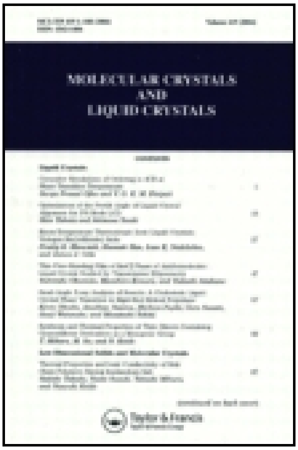

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A Simple Statistical-Thermodynamical Model for Liquid-Crystalline Polymers with Repeating Units Comprising a Rigid and a Flexible Part

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A Simple Statistical-Thermodynamical Model for Liquid-Crystalline Polymers with Repeating Units Comprising a Rigid and a Flexible Part[†]

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A statistical-thermodynamical model of liquid crystalline polymers in which the repetitive units comprise a rigid and a flexible part is presented. Features of the model are: (i) the steric contribution to the entropy is evaluated according to Di Marzio, and (ii) the conformational contribution is obtained through a simple matrix multiplication scheme allowing its evaluation as a function of the order parameter, temperature, length of the flexible and of the rigid parts. The trends experimentally observed for various polymers are correctly reproduced. The results of various sample calculations will be shown.

INTRODUCTION

Available theories of the thermodynamic properties of mesogenic materials rest essentially on the hypothesis that individual molecules may be treated either as single rigid rods, as single rigid rods with pendant flexible chains, or as semiflexible chains with continuous flexibility. The first two treatments have been successfully applied[1-3] to a wide class of low molecular weight compounds, predicting both the existence of a stable nematic phase at the melting point and the order of magnitude of many thermodynamic parameters relating to the isotropic-nematic transition. The hypothesis of continuous flexibility has been recently used to explain the experimental finding[4] that PTFE melts to a nematic phase and to predict a hypothetical isotropic-nematic transition[5] for PE at 74.6 K. Apart from a limited number of cases, however, polymers giving stable liquid crystalline phases are constituted either by flexible chains with pendant rigid groups or by the alternation of flexible and rigid parts in the chain backbone. The phase behavior of polymers of the first kind has been thoroughly investigated;[6,7] mesogenic polymers of the latter kind have been more recently prepared and characterized, for instance, by Roviello and Sirigu[8,9] and by Blumstein.[10]

We present in this paper a statistical thermodynamical lattice model of mesogenic polymers of the second kind which takes into account both the short-range statistics of real molecules and the dependence of the orientational and conformational partition function on the directional constraints present in nematic phases.

Our treatment, though still crude and constrained to a lattice, gives rise to reasonable predictions and may be further extended to incorporate useful features from previous approaches.

In this paper, we will confine our attention to the results that can be obtained for the case of polymers constituted by the alternation of flexible and rigid parts of fixed length and for the corresponding monomers.

THE MODEL

We consider a nematic domain constituted by $n_0 = xn_2 + n_1$ sites of a lattice with coordination number z, containing n_2 chain molecules of $x - 1$ segments each and n_1 solvent molecules or empty sites. The nematic director is identified with the lattice direction z and $\alpha_{z,i}$ is the fraction of i-th segments in this direction.

The total partition function for the domain can be written as:

$$Z_t = Z_{\text{conf}} Z_{\text{st}} Z_{\text{en}} \tag{1}$$

where Z_{conf} represents the orientational and conformational partition function for a set of n_2 solute molecules, while Z_{st} and Z_{en} are contributions deriving from the need that two segments do not contemporarily occupy the same lattice site and from the orientation-dependent part of the interaction energy among segments, respectively.

Z_{conf} is formulated, in the absence of directional constraints (isotropic case), as the product:

$$Z_{\text{conf}} = \left\{ \mathbf{J} \left(\prod_{i=1}^{x-1} \mathbf{U}_i^0 \right) \mathbf{J}^* \right\}^{n_2} \tag{2}$$

where $\mathbf{J}$ and $\mathbf{J}^*$ are the row and column vectors

$$\mathbf{J} = \begin{vmatrix} 1 & 0 & \dots \end{vmatrix} \qquad \mathbf{J}^* = \begin{vmatrix} 1 \\ 1 \\ \vdots \end{vmatrix}$$

of the same order of $\mathbf{U}_i^0$; the latter contains statistical weights relating the possible orientational and conformational states of segment i to those of segment $i - 1$. In the cubic lattice, for instance, in the simple case where the allowed states are identified with lattice directions (and hence in the absence of correlations between neighboring segments within the chains, but for the prohibition of direction reversals and the ε_i factors),

$$\mathbf{U}_i^0 = \begin{array}{c|ccc|} & z & x & y \\ z & 1 & 2\varepsilon_i & 2\varepsilon_i \\ x & 2\varepsilon_i & 1 & 2\varepsilon_i \\ y & 2\varepsilon_i & 2\varepsilon_i & 1 \end{array} \tag{3}$$

where $\varepsilon_i = \exp(-T_i^0/T)$ is a factor taking into account the energy RT_i^0 required to bend the chain between segments $i - 1$ and i (of course, $T_1^0 = 0$).

One or more constraints can be introduced in the evaluation of Z_{conf} with some modification of the method given by Allegra for polymer chains with neighbor interactions. According to this method,[11,12] the constrained partition function for the previous example under the single linear condition that the average fraction of segments along z be a given value, $\overline{\alpha}_z$, becomes

$$Z_{\text{conf}} = \beta^{-(x-1)\overline{\alpha}_z n_2}\left\{\mathbf{J}\left(\prod_{i=1}^{x-1}\mathbf{U}_i\right)\mathbf{J}^*\right\}^{n_2} \tag{4}$$

where $\mathbf{U}_i$ corresponds to $\mathbf{U}_i^0$ of Eq. 2 in which columns pertaining to the z direction have been multiplied by β; the value of β to be introduced in Eq. 4 is the one which makes the distribution of orientations to assume the given $\overline{\alpha}_z$.

In practice, it is convenient to assign a value to β and to evaluate the corresponding $\overline{\alpha}_z$ as:

$$\overline{\alpha}_z = (x - 1)^{-1}\sum_{i=1}^{x-1}\alpha_{z,i}$$

where

$$\alpha_{z,i} = \frac{\mathbf{J}(\prod_{k=1}^{i-1}\mathbf{U}_k)\mathbf{U}_i^*(\prod_{n=i+1}^{x-1}\mathbf{U}_n)\mathbf{J}^*}{\mathbf{J}(\prod_{m=1}^{x-1}\mathbf{U}_m)\mathbf{J}^*}$$

with $\mathbf{U}_i^*$ being the matrix $\mathbf{U}_i$ in which all terms but those pertaining to the z column have been substituted by zeros.

For the purpose of the present paper, the polymer chains are considered to have "repeating units" constituted by f "flexible" segments (i.e. segments with $\varepsilon_i \neq 0$) and a "rigid group" (i.e. a group comprising a segment with $\varepsilon_i \neq 0$ followed by a sequence of $r - 1$ segments with $\varepsilon_i = 0$; see

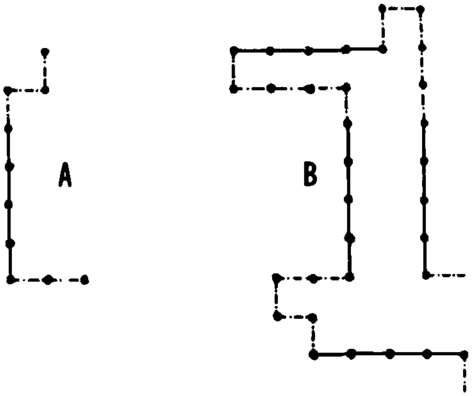

FIGURE 1 Model drawing of a monomer (A) and a polymer (B) "molecule" with r = W, $f = 5(4R\text{-}5F)$ in a bidimensional square lattice. Rigid groups, full line; flexible parts, broken line.

Figure 1). The general symbol $rR\text{-}fF$ will now be used to denote such a constitution. A formulation similar to that of Eq. 4 allows further constraints to be introduced, when needed. For instance, the constrained Z_{conf} under the two contemporary linear conditions that the average fraction along z of rigid and flexible segments assume the given values $\overline{\alpha}_{z,r}$ and $\overline{\alpha}_{z,f}$, respectively, can be evaluated as:

$$Z_{\mathrm{conf}} = \beta_r^{-(x-1)q_r\alpha_{z,r}n_2} \cdot \beta_f^{-(x-1)q_f\alpha_{z,f}n_2} \cdot \left\{\mathbf{J}\left(\prod_{i=1}^{x-1}\mathbf{U}_i\right)\mathbf{J}^*\right\}^{n_2} \qquad (5)$$

where the U_i's are multiplied in the z columns by the appropriate β_r or β_f factors and $q_r = r/(r+f)$, $q_f = f/(r+f)$.

For linear chains, as those considered in this paper, the expression of Di Marzio[12] for Z_{st} appears to be fully adequate. Hence we use:

$$\begin{aligned} \ln Z_{\mathrm{st}} = {} & -n_2 \ln(v_2/x) - n_1 \ln v_1 + n_0(1 - \overline{\alpha}_z v_2(x-1)/x) \ln(1 - \overline{\alpha}_z v_2 \\ & (x-1)/x) + n_0[(z-2)/2)(1 - (1 - \overline{\alpha}_z)v_2(x-1)2/(z-2)x] \\ & \ln(1 - (1 - \overline{\alpha}_z)v_2(x-1)2/(z-2)x) \end{aligned} \qquad (6)$$

where $v_2 = xn_2/n_0$ and $v_1 = 1 - v_2$.

According to Ronca and Yoon,[5] the orientation-dependent part of the interaction energy among neighboring segments can be taken into account for continuously flexible chains, writing:

$$\ln Z_{\mathrm{en}} = (1/2)xn_2(T^*/T)\overline{s}^2 \qquad (7)$$

where T is the temperature, T^* measures the orientation-dependent interaction energy and $\overline{s}$ is the order parameter of the domain in the z direction.

For chain molecules with alternating rigid and flexible segments, on the hypothesis that relevant (but at any rate small, in our approximation) interactions take place among rigid groups only; we write:

$$\ln Z_{\mathrm{en}} = (1/2)xn_2(T^*/T)q_r^2\bar{s}_r^2 v_2 \tag{8}$$

where $\bar{s}_r = (z/(z - 2))(\overline{\alpha}_{z,r} - 2/z)$ is the order parameter for the rigid groups (when $z = 6$, $\bar{s}_r = (3/2)\overline{\alpha}_{z,r} - 1/2$).

RESULTS AND DISCUSSION

Equations 4 to 8 of the previous section show that in the general case, the total partition function for the domain, Z_t depends on both the average orientations along the director of the flexible and rigid parts, requiring that Eq. 5 be used to evaluate Z_{conf}.

When, however, $Z_{\mathrm{en}} = 1$ (i.e. in the limit of very high temperatures, the athermal case) only the average $\overline{\alpha}_z = (r\overline{\alpha}_{z,r} + f\overline{\alpha}_{z,f})/(r + f)$ needs to be specified, and Eq. 4 provides the maximum value of Z_{conf} for the given average orientation.

Figure 2 shows a map of $g/RT = -(\ln Z_t)/n_0$ against the order parameters of the rigid and flexible parts, $\bar{s}_r$ and $\bar{s}_f$ respectively, evaluated for the polymer $3R$-$2F$ at $T \rightarrow \infty$, $v_2 = 1$ (and $Z = 6$) by use of Eqs. 5 and 6. Our calculation is seen to provide separate minima for the (metastable) isotropic liquid and a stable nematic phase with highly aligned rigid groups and much less oriented flexible parts. The dotted line, which has been obtained by use of Eqs. 4 and 6, corresponds for each average order parameters $\bar{s}$ to the map point which makes Z_t a maximum.

The value of g/RT for various polymers with constitution $3R$-fF and for the corresponding monomers is plotted in Figure 3 against $\bar{s}$. A stable ordered liquid phase is found for polymers with $f = 1$ and $f = 2$ only, while monomers with the same constitution are predicted to be isotropic in the given conditions ($T \rightarrow \infty$, $v_2 = 1$ and $Z = 6$).

Figure 4 compares the free energy difference between metastable isotropic liquid and stable nematic phase for a series of polymers and monomers with varying constitution. The curves of Figures 3 and 4 allow the following assertions to be made:

a) for a given length of the flexible parts, longer rigid groups tend to stabilize the anisotropic phase;

b) for a given length of the rigid groups, longer flexible parts favor the isotropic liquid;

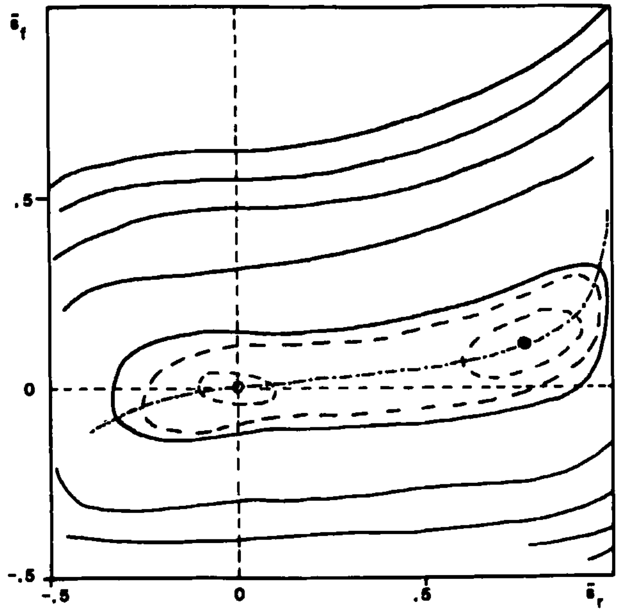

FIGURE 2 Map of $g/RT = -\ln(Z_i)/n_0$ against the order parameters of the rigid ($\bar{s}_r$) and flexible ($\bar{s}_f$) parts for the 3*R*-2*F* polymer ($T \rightarrow \infty$, $v_2 = 1$, $Z = 6$). Full line curves drawn at 0, −0.04, −0.08, −0.12, −0.16; broken curves at −0.164 and −0.168. Local minimum at −0.1686 for the isotropic liquid; absolute minimum at −0.1696 ($\bar{s}_r = 0.76$, $\bar{s}_f = 0.11$) for the nematic phase. The dotted line has been evaluated using Eqs. 4 and 6 (see text).

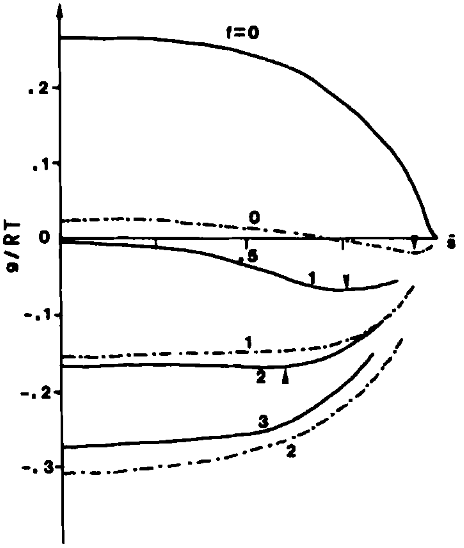

FIGURE 3 Plot of g/RT for polymers (full lines) and monomers (broken lines) 3*R*-*fF* vs the average order parameter $\bar{s}$. $T \rightarrow \infty$, $v_2 = 1$, $Z = 6$.

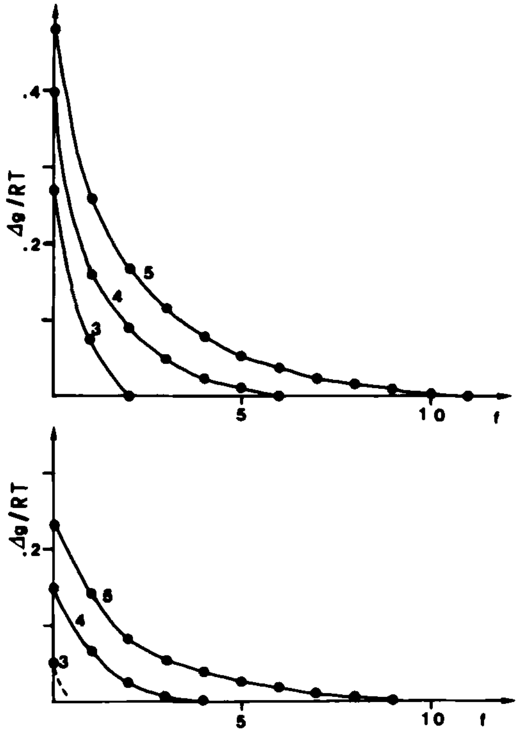

FIGURE 4 Difference of g/RT between stable anisotropic phases and the isotropic liquid for polymers (upper plot) and monomers (lower plot) with various constitutions as a function of the length, f of the flexible parts. The length, r of the rigid groups is indicated near each curve. $T \rightarrow \infty$, $v_2 = 1$, $Z = 6$.

c) the length of the flexible parts required to bring the isotropic and anisotropic phases to an equilibrium is an increasing function of the length of the rigid groups;

d) the liquid crystalline phase is always more favored for polymers than for the corresponding monomers;

e) differences in the behavior of polymers and monomers are mostly found in the low r, low f range.

Figure 5 plots the order parameters $\bar{s}_r$, $\bar{s}_f$ and $\bar{s}$ for $4R$-fF polymers and monomers vs the length, f of the flexible parts in the range of stability of the nematic phase. The ordering of the rigid groups is seen to be always high, whereas that of the flexible segments is much smaller and decreases with increasing f. Polymers are always more ordered than the corresponding monomers.

Extension of the model to the thermal case requires that T^0 and T^* (see Eqs. 3 and 8) be selected in a reasonable range. Figures 6 and 7 show, as

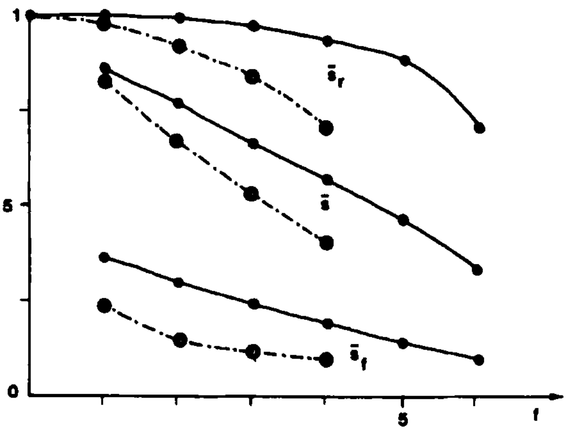

FIGURE 5 Plot of the order parameters $\bar{s}_r$, $\bar{s}_f$ and $\bar{s}$ for 4*R*-*fF* polymers (full lines) and monomers (broken lines) vs the length, *f* of the flexible parts.

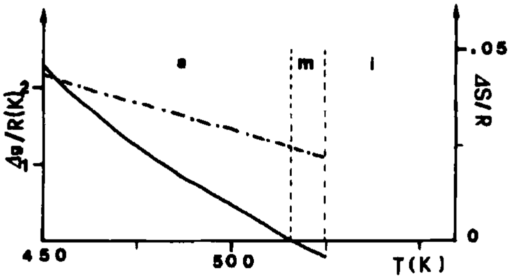

FIGURE 6 Difference of free energy (full line, left scale) and entropy (broken line, right scale) between anisotropic and isotropic phases for the 3*R*-4*F* polymer as a function of temperature. $T^0 = 250$ K, $T^* = 222$ K, $v_2 = 0.9$, $Z = 6$. a) range of stability of the nematic phase; m) isotropic phase stable, nematic metastable, i) isotropic phase stable, no minimum found for a nematic phase.

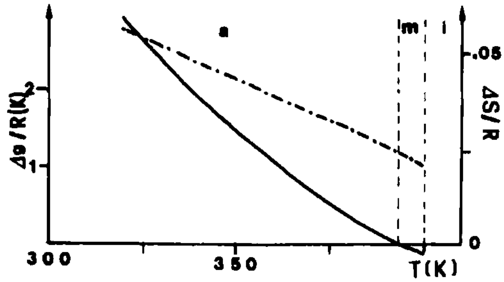

FIGURE 7 Same as Figure 6 for the 3*R*-4*F* monomer as a function of temperature.

an example, the free energy and entropy differences (per mol of units) between the isotropic and nematic phase for the polymer 3*R*-4*F* and its monomer as a function of the temperature. Curves were obtained with T^0 = 250 K, T^* = 222 K, v_2 = 0.9 and Z = 6. The equilibrium temperatures divide the Helmholtz free energy plots in two regions, defining the range of absolute stability of the nematic (left) and isotropic (right) phases at constant volume. The nematic phase is metastable in a small range of temperatures following isotropization, after which the corresponding minimum disappears. The polymer is seen to undergo the isotropic to nematic transition at around 515 K, with an entropy of the order of 0.025 R per mol of units. The same transition is found for the monomer at around 395 K, with a similar transition entropy.

A map of g/RT against $\bar{s}_r$ and $\bar{s}_f$ at a temperature slightly above isotropization is shown for the polymer 3*R*-4*F* in Figure 8; the map region comprising the metastable liquid crystalline phase and the stable isotropic liquid is seen to be surprisingly flat, showing that small external forces can have a decisive influence on their relative stability.

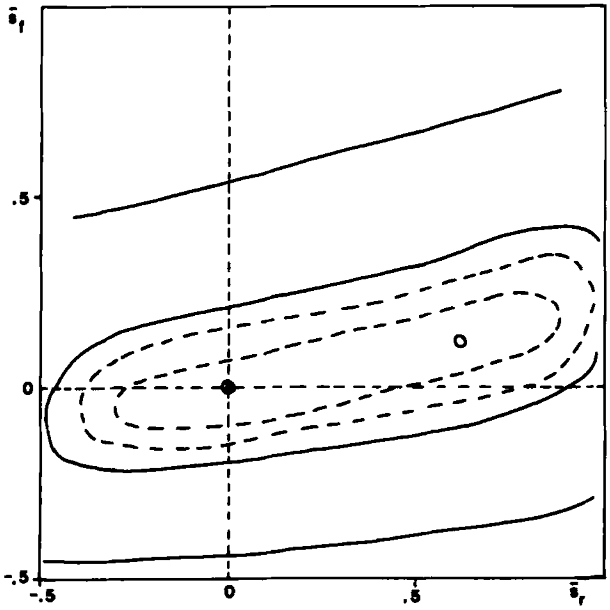

FIGURE 8 Map of g/RT against $\bar{s}_r$ and $\bar{s}_f$ for the 3*R*-4*F* polymer at 520 K with T^0 = 250 K, T^* = 222 K, v_2 = 0.9, Z = 6. Full curves drawn at −0.200 and −0.300; broken curves at −0.310 and −0.315; absolute minimum at −0.3194 for the isotropic liquid and relative minimum at −0.3193 for the metastable nematic phase ($\bar{s}_r$ = 0.62, $\bar{s}_f$ = 0.12).

The temperature dependence of the order parameters is plotted in Figure 9 for both the polymer and the monomer 3*R*-4*F*; the average order parameter is seen to rise at the transition point from zero to about 0.4 and to increase smoothly in the range of stability of the ordered phase. Figure 10 shows the variation of the segment order parameter along the polymer chain at the isotropic to nematic transition temperature: apart from the chain termini, having slightly higher values of s_i, flexible segments immediately adjacent to rigid groups are less oriented than the central ones,

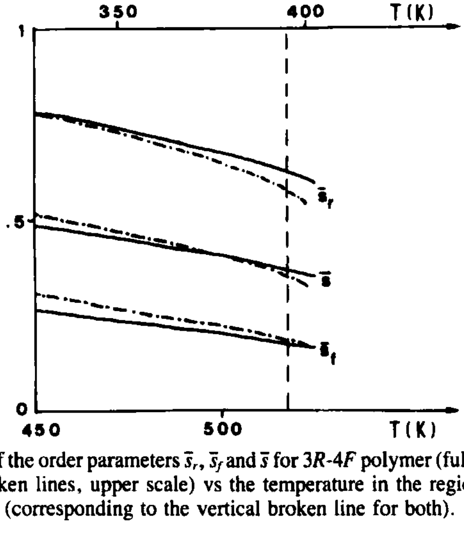

FIGURE 9 Plot of the order parameters $\bar{s}_r$, $\bar{s}_f$ and $\bar{s}$ for 3*R*-4*F* polymer (full lines, lower scale) and monomer (broken lines, upper scale) vs the temperature in the region of the isotropic-nematic transitions (corresponding to the vertical broken line for both).

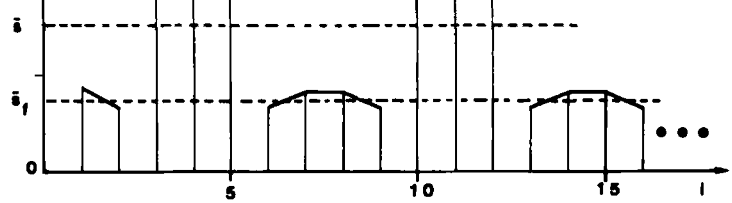

FIGURE 10 The dependence of the segment order parameter s_i on the position *i* of the segment along the 3*R*-4*F* polymer chain at the isotropic-nematic transition point.

whereas the order parameters of segments belonging to rigid groups are constant along the chains.

CONCLUSIONS

The results given in the previous section for polymers constituted by the alternation of rigid and flexible parts show that the behavior of polymers is not much different from that of the corresponding monomers; the differences occur mostly in the low r, low f range. For instance, in the athermal $4R$-fF case and with identical approximations, a liquid ordered phase is predicted to occur when $f \leqslant 6$ for high molecular weight polymers and when $f \leqslant 4$ for the corresponding monomers. In the athermal rR-$2F$ case, the anologous limits are $r > 2$ for polymers and $r > 3$ for monomers.

A shift of the stability range of the nematic phase to higher temperatures is predicted in the thermal case for polymers with respect to monomers, the shift being of the order of magnitude which is experimentally observed.

We have thus shown that lattice models can be extended to polymers with flexible and rigid sections alternating along the chain backbone. The usage of matrix methods, exemplified in this paper in the most simple cases, provides in our view of general way of getting rid of cumbersome combinatorial expressions and of evaluating easily various kinds of distribution. With the calculation method used, it is easy to make predictions about the behaviors of monomers, oligomers and polymers of any specified constitution (and hence copolymers, mixtures of polymers with different molecular weights and so on). Also, the method lends itself to easy extension to the case of oligomers and polymers (like poly-amino acids), in which the length of the rigid portions may be varied according to a conformational equilibrium. Extensions to still other systems (e.g. polymers with rigid side chain groups) are presently under investigation in our laboratory.

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