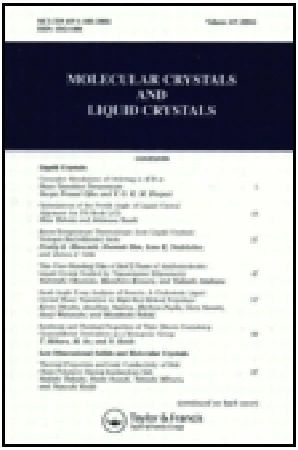

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Conformation of LC Side Chain Polymers in the Smectic Phase

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CONFORMATION OF LC SIDE CHAIN POLYMERS IN THE SMECTIC PHASE

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ABSTRACT Four models for the conformation of the backbone of a LC side chain polymer in the smectic phase are proposed. The models differ with respect to the assumed conformational behaviour of the backbone in the planes between the smectic lamellae. Thermally activated crossing of the backbone through the lamellae (equilibrium effect) as well as entanglement induced crossing (non-equilibrium effect) is considered. The ratio of the radii of gyration normal and perpendicular to the director of the side chains is derived and it is shown how this ratio depends on temperature in the equilibrium model.

INTRODUCTION

The phase behaviour of liquid crystalline side chain polymers (LSP) has been subject to many experiments during the last years[1,2]. Some of these LSP systems exhibit a smectic phase. The smectic lamellae are built by the mesogenic side chains which are connected via a flexible spacer with the polymeric backbone (BB). The BB is assumed to be located mainly in the interlamellar regions.

A SANS experiment[3] showed the existence of a non-vanishing radius of gyration normal to the smectic planes. Thus there must exist crossings of the BB through the lamellae. Such a crossing might be either a thermally activated state (equilibrium state) or it might be induced by an entanglement which prevents the BB on the time scale of experiment from reaching its ground state (non-equilibrium effect). Both cases will be discussed below.

The main question we are concerned with is: What kind of conformation does the BB assume between two crossings?

As usual[4] the BB is described by some type of random walk (RW). With the exception of one model all RWs are placed on an anisotropic lattice with lattice spacing (Kuhn step length) a and coordination number q_o in the interlamellar planes (xy-plane) and step length Da in the z direction, see Figure 1. When considering equilibrium effects a crossing needing D steps is weighed by a factor exp(-E/kT) where E is the free energy of one crossing.

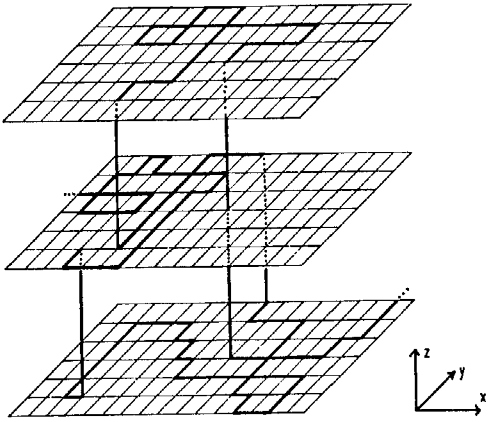

FIGURE 1. Conformation of one backbone in the PRW model. The side chains which fill the space between the planes are omitted for the sake of clearness.

We propose now a hierarchy of models for the type of RW in the xy-plane. In the following v_k is the number of possible configurations of a BB segment with k RW steps between two crossings.

1. Pure RW (PRW)

$$v_k = q_0^k \tag{1}$$

2. Self-avoiding walk (SAW)

$$v_k = q_1^k k^{\gamma-1} \tag{2}$$

q_1 is an effective coordination number with $1 < q_1 < q_o$ and γ is an universal exponent given in two dimensions (2-D) by $\gamma = 4/3$ [4].

3. Compact SAW (CAW)

$$v_k = q_2^k \tag{3}$$

q_2 is another effective coordination number $(1 < q_2 < q_o)$. Eq. (3) has been derived for closed CAW but it has been suggested that for large k Eq. (3) also holds for open CAW[5].

4. Straight walk (SW)

$$v_k = 2 \tag{4}$$

The models are ordered in such a way that the number of degrees of freedom decreases from the highest possible value in the PRW model to the lowest possible one in the SW model. There is of course a variety of types of RWs not listed above. But all these types are intermediate between the PRW and the SW with respect to their number of degrees of freedom.

In the next section we sketch how the method of generating functions (GF) is used to calculate the mean squared end-to-end distances r_z^2 and $r_\perp^2$ in the z direction and in the xy-plane and hence the appropriate radii of gyration R_z^2 and $R_\perp^2$ for any type of RW for which v_k depends on k. The SW case needs a different formalism. It is appropriate to leave the lattice model and to describe this case by a kind of 2-D Pearson RW with Poisson step length distribution, see Figure 2.

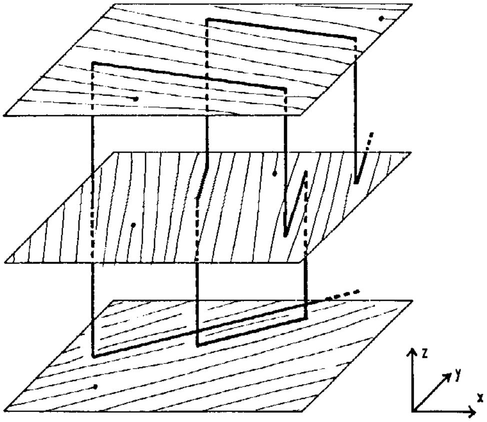

FIGURE 2. Conformation of one backbone in the SW model. To make clear the sheaflike structure also other BBs are depicted. The lamellar thickness is highly exaggerated.

As we are interested in the fundamental results emerging from the models only the case of very long BBs is considered. Besides that it is assumed that the crossing energy E is large, i.e. exp(-E/kT) ≪ 1. Under these assumptions the following relation can be used

$$R_z^2/R_\perp^2 \cong r_z^2/r_\perp^2 =: b \, . \qquad (5)$$

THE METHOD OF GENERATING FUNCTIONS

This method is a useful tool to derive the partition function Q_n of many types of RWs with step number n [6]. The GF for one crossing U(x) and the GF for a lattice walk between two crossings V(x) are given by

$$U(x) = 2x^D \exp(-E/kT) \qquad (6)$$

$$V(x) = \sum_{l=0}^{\infty} v_l x^l . \qquad (7)$$

x is a dummy variable and the coefficients v_l are defined in Eqs. (1) - (3) for PRW, SAW, and CAW, respectively. The GF containing complete information about all configurations for all walk lengths is given by

$$G(x) = \sum_{l=0}^{\infty} (U(x)V(x))^l . \qquad (8)$$

For $n \gg 1$ the following relation holds

$$Q_n \simeq x_o^{-n} , \qquad (9)$$

where x_o is the pole of least modulus of G(x). The average number of steps being involved in crossings is given by

$$n_z = kTD \frac{\partial \ln Q_n}{\partial E} n . \qquad (10)$$

The behaviour of the BB in the z direction can be modelled by a 1-D RW with step length Da and step number n_z. The average number of steps in the xy-plane is $n_\perp = n - n_z$. From this the anisotropy factor b as defined in Eq. (5) is readily calculated [7]. The result for the PRW is given below. The results for the SAW and the CAW will be given elsewhere [7].

INTERLAMELLAR SW

As the directions of the SWs belonging to one BB are assumed to be randomly distributed in different planes, see Figure 2, it is possible to use the concept of 2D Pearson RW[8] (reentrant correlation effects are neglected). Since the BB has no degrees of freedom except the possibility of generating crossings the average number c of crossings for a BB with length na obeys

$$c = n \exp(-E/kT) \, . \tag{11}$$

The crossings are randomly distributed along the BB. So the probability density function for the distance r between two crossings is given by

$$p(r) = \exp(-mr)/m \quad , \tag{12}$$

where $m = c/na$. $r_{\perp}^2$ can be evaluated by the method of characteristic functions[7] and is given by

$$r_{\perp}^2 = 2na^2 \exp(-2E/kT) \left[1 - D \exp(-E/kT) \right] . \tag{13}$$

The anisotropy factor is given below.

ENTANGLEMENT INDUCED CROSSING

In the preceding two sections it was assumed that all LSPs in the sample have time to reach the equilibrium state. But it is well known from polymer physics that systems with long chains are trapped upon cooling in non-equilibrium states, due to entanglements and other effects which have kinetic origin. Similar problems presumably occur in LSP systems in a sharpened form because of the difficulty of untiing entanglements, see Figure 3.

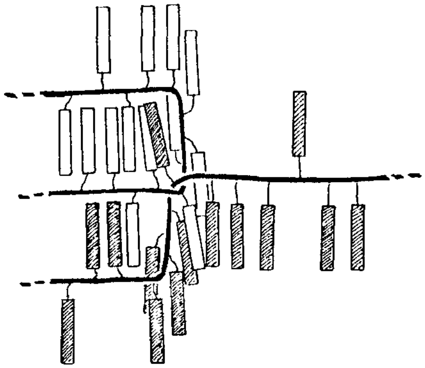

FIGURE 3. A typical entanglement. Some of the side chains are depicted to show the distortion of the smectic lamellae by the induced crossing.

In order to calculate the effects of such trapped entanglements thermally activated crossings are ignored and it is assumed that a crossing is induced by an entanglement (or by several entanglements) preventing the BB from reaching its equilibrium conformation. Again PRW, SAW, CAW, and SW behaviour might occur between two crossings. Presently we assume that the probability p of finding an entanglement is constant along the BB. Now Eq. (12) is valid for all RW types with r being the curvilinear distance between two crossings. If we choose for E/kT a value in such a way that p = m holds we can use the results derived above also for the non-equilibrium problem.

RESULTS AND DISCUSSION

The anisotropy factor b for the two extreme models (PRW, SW) is for the equilibrium state approximately given by

$$b_{PRW} = 2D^2 4^{-D} \exp(-E/kT) \qquad (14)$$

$$b_{SW} = (D^2/2)\exp(-3E/kT) \quad , \qquad (15)$$

where we have set $q_o=4$ for the PRW. It follows immediately that it is impossible to decide from a knowledge of the anisotropy factor measured by SANS experiment which of the RW models is the right one as long as nothing is known about the magnitude of the crossing energy E. In case a temperature dependence will be measured in a future experiment the equilibrium model has to be prefered since the number of entanglement induced crossings is independant of temperature.

There is some evidence in favour of the SW model due to SAXS experiments[9,10] which were performed on LC side chain oligomers. But as is known from polymeric systems the behaviour of oligomers upon cooling differs drastically from that of long polymers because of kinetic effects. The same might be true for LSP systems due to disentangling problems which occur in a sharpened form there.

In conclusion it can be stated that the SW model with entanglement induced crossings appears to be the most useful to explain both SANS and SAXS experiments.

Finally we point out that the main reason to introduce the method of GF, despite the fact that theoretical approaches considering PRW behaviour exist[11,12], is based on the following argument: in case future experiments suggest a BB conformation with a behaviour intermediate between PRW and SW this can be readily taken account of if the appropriate relation between step number and number of configurations of a segment is approximately known.

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