# Conformations of comb-like macromolecules in a nematic phase The interpretation of small angle neutron scattering data

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The experimental data of Kirste and Ohm (1985, *Makromolec. Chem. rap. Commun.*, **6**, 179) and of Keler *et al.* (1985, *J. Phys. Lett., Paris*, **46**, 1065) show that the mesogenic units tend to be perpendicular to the backbone segments in thermotropic liquid-crystalline polymers. Using a simple model (a comb-like freely jointed chain) an estimate is made for the second moment of the distribution of mesogens with respect to the backbone.

## 1. Introduction

At present there is a growing interest in the study of liquid-crystalline polymers. Comb-like polymers with mesogenic molecules represent a large class of polymers which display liquid-crystalline properties. Extensive information is available on the properties of such polymers both in dilute solutions and in the bulk phase [1–6]. Studies of liquid-crystalline polymers with mesogenic units in the bulk were performed by various methods, such as X-ray scattering and diffraction, N.M.R. spectroscopy and optical diffraction. These measurements were mainly concerned with the ordering of the mesogenic units and structural changes at the phase transitions [1–6]. However, the conformation of the main macromolecular chain was not studied.

The labelling method allows the extraction of direct information on the conformation of a single macromolecule, in the bulk, from neutron scattering data [7, 8]. Recent experiments based on small-angle scattering and neutron diffraction have clarified the conformation of the main chain of macromolecules in mesophases [9, 10]. The square root of the mean square projection of the radius of gyration of the main chain parallel $R_{\parallel}$ and perpendicular $R_{\perp}$ to the axis of orientation are found to be $9\cdot4 \pm 0\cdot5$ nm and $11\cdot8 \pm 0\cdot6$ nm, respectively [9]. The anisotropy parameter was determined to be

$$a = \frac{R_{\perp}}{R_{\parallel}} = 1\cdot25, \tag{1}$$

and a value of $1\cdot1$ has been found for the other polymer. The mean square radius of gyration for the macromolecular coil of the main chain

$$R_g^2 = R_{\parallel}^2 + 2R_{\perp}^2 \tag{2}$$

increases slightly on passing from the isotropic to the nematic phases.

## 2.  Qualitative considerations

There are numerous experimental data which testify to the existence of intramolecular order in comb-like macromolecules in dilute solutions [2, 4]. Side groups of such macromolecules have an orientation perpendicular to the main chain. This intramolecular order vanishes on going from a dilute solution to the concentrated one [11], but a tendency of the side mesogenic units of the comb-like polymers to become perpendicular to the main chain remains even in the bulk, as follows from experiment.

Consider comb-like polymers in the nematic phase. We can give two main reasons for the orientation of the mesogenic units. The first is the interaction of neighbouring mesogenic units with each other in the chain, and also the interaction of these units with the main backbone. We call the distribution function of the orientation of the mesogenic units relative to segments of the central backbone, determined by such interactions, the primary one. The second reason is the nematic ordering. Actually, its existence is accompanied by a large number of contacts between the mesogenic units, which results in the exclusion of the main backbone from the region of contacts. This element of separation is displayed completely in a smectic phase, where the liquid-crystalline polymer is arranged in layers with the formation of a layer of mesogenic units and an intermediate layer containing fragments of the main backbone.

The methods of polymer conformational statistics now developed [12–14] allow us in principle to calculate the primary function of the mesogenic units, orientational distribution. Theoretical calculations of the contribution of the nematic ordering to the mesogenic distribution function has not yet been achieved. Theoretical calculation of the distribution function is not the subject of this paper. However by using experimental data and a simple model for the chain (a comb-like freely jointed chain) we do determine the second moment of the distribution function.

## 3.  Comb-like freely jointed chain

A comb-like freely jointed chain (cf. figure) is a modification of the well-known Kuhn freely jointed chain. Each segment of this chain is characterized by two unit
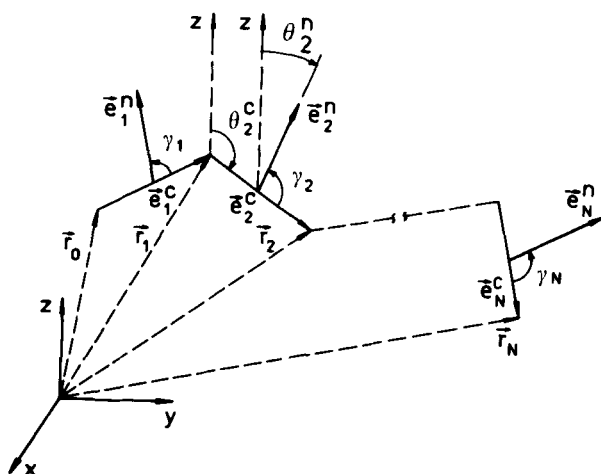


The model of a comb-like freely jointed chain. A segment of this chain is characterized by two unit vectors $e^h$ and $e^c$ directed along the mesogen and along the Kuhn segment in the main chain, respectively.

vectors $\mathbf{e}^n$ and $\mathbf{e}^c$ directed along the mesogenic unit and along the Kuhn segment, respectively. The correlation between the mesogen and the backbone is determined by an $f$ function distribution, depending on the angles between $\mathbf{e}^n$ and $\mathbf{e}^c$ in each segment. Orientations of the $\mathbf{e}_i^n$ vectors in an isotropic phase are random. In a nematic phase the distribution of $\mathbf{e}_i^n$ is anisotropic and depends on the angle $\theta_i^n$ between $\mathbf{e}_i^n$ and the direction of the nematic director [15]. The probability of a particular conformation of the chain is given by

$$\varrho(\Omega_1^n, \Omega_1^c, \ldots, \Omega_N^n, \Omega_N^c) \;=\; \prod_{i=1}^{N} g(\cos\theta_i^n) f(\cos\gamma_i) d\Omega_i^n d\Omega_i^c / Z, \tag{3}$$

where

$$d\Omega \;=\; \sin\theta d\theta d\phi, \quad \cos\gamma_i \;=\; \mathbf{e}_i^n \cdot \mathbf{e}_i^c$$

and $Z$ is the partition function which is the result of integration of the numerator in equation (3) over all the angles. The mesogen distribution $g$ is an even function, as is well known.

The distribution is not available from experiment, but its second moment, or the order parameter,

$$S^n \;=\; \int_0^\pi g(\cos\theta^n)(3\cos\theta^n - 1)/2 \sin\theta^n d\theta^n, \tag{4}$$

is. We shall assume that the distribution function $f(\cos\gamma)$ has a maximum at $\gamma = \pi/2$ and is an even function. The order parameter of the segments of the main chain can be determined in the usual way from

$$S^c \;=\; (3\overline{\cos^2\theta^c} - 1)/2 \;=\; \frac{\displaystyle\int_0^\pi g(\cos\theta^n) f(\cos\gamma) P_2(\cos\theta^c) d\Omega^n d\Omega^c}{\displaystyle\int_0^\pi g(\cos\theta^n) f(\cos\gamma) d\Omega^n d\Omega^c} \tag{5}$$

where $P_2(\cos\theta)$ is the second order Legendre polynomial.

It is convenient to expand $f(\cos\gamma)$ in a series of the Legendre polynomials and then to represent each polynomial through spherical harmonics by means of the spherical harmonic addition theorem. The result can be written as

$$S^c \;=\; S^n S^f \tag{6}$$

where $S^n$ is given by equation (3) and $S^f$ by the

$$S^f \;=\; \int_0^\pi f(\cos\gamma) P_2(\cos\gamma) \sin\gamma d\gamma \Big/ \int_0^\pi f(\cos\gamma) \sin\gamma d\gamma. \tag{7}$$

The value $S^f$ can be called the order parameter defined by the distribution function $f$. Later on we shall need the mean square of the vector projections of $\mathbf{e}^c$. They may be expressed by the order parameter

$$\overline{(\mathbf{e}_\parallel^c)^2} \;=\; \overline{\cos^2\theta^c} \;=\; (1 + 2S^c)/3, \tag{8}$$

$$\overline{(\mathbf{e}_{\perp_1}^c)^2} \;=\; \overline{(\mathbf{e}_{\perp_2}^c)^2} \;=\; \tfrac{1}{2}\overline{\sin^2\theta^c} \;=\; (1 - S^c)/3. \tag{9}$$

The subscript $\parallel$ in equation (8) means a projection on the axis parallel to the nematic director, and subscripts $\perp_1$ and $\perp_2$ in equation (9) denote perpendicular projections on the nematic director.

## 4.    The neutron cross section

We now calculate the neutron cross section of the comb-like freely jointed chain under the assumption that the scattering centres are at the ends of the segments (their radius vectors are shown in the figure). The mean square of the projection of the vector $\mathbf{r}_j - \mathbf{r}_i$ on the direction parallel of the nematic director can be written as

$$\overline{(\mathbf{r}_j - \mathbf{r}_i)_{\parallel}^2} = b^2 \sum_{K=i+1}^{j} \overline{(\mathbf{e}_{K,\parallel}^c)^2} = b^2 \overline{(\mathbf{e}_{\parallel}^c)^2} |j - i|, \tag{10}$$

where $b$ is the Kuhn segment value of the freely jointed chain. Analogous expressions can be written for other projections. The mean square projections of the Kuhn segment can be written as

$$b_{\parallel}^2 = \overline{(\mathbf{e}_{\parallel}^c)^2} b^2, \; b_{\perp_1}^2 = \overline{(\mathbf{e}_{\perp_1}^c)^2} b^2 \; \text{and} \; b_{\perp_2}^2 = \overline{(\mathbf{e}_{\perp_2}^c)^2} b^2 \tag{11}$$

It is well known that the cross-section for elastic coherent scattering for one macro-molecule is

$$\sigma \sim \sum_{k,j=1}^{N} \exp\{i(\mathbf{Q} - \mathbf{Q}_0)\cdot(\mathbf{r}_K - \mathbf{r}_j)\}, \quad |\mathbf{Q}| = |\mathbf{Q}_0|, \tag{12}$$

where $\mathbf{Q}_0$ and $\mathbf{Q}$ are the wavevectors for incident and scattered neutrons, respectively. Expanding the exponential function in a series, under the assumption of small-angle scattering and considering just the first and second terms, we obtain

$$\sigma \sim N^2 \left\{ 1 - \frac{1}{2N^2} \sum_{i,j=1}^{N} [(\mathbf{Q} - \mathbf{Q}_0)_{\parallel}^2 \overline{(\mathbf{r}_i - \mathbf{r}_j)_{\parallel}^2} \right.$$
$$\left. + (\mathbf{Q} - \mathbf{Q}_0)_{\perp_1}^2 \overline{(\mathbf{r}_i - \mathbf{r}_j)_{\perp_1}^2} + (\mathbf{Q} - \mathbf{Q}_0)_{\perp_2}^2 \overline{(\mathbf{r}_i - \mathbf{r}_j)_{\perp_2}^2}] \right\}. \tag{13}$$

The indices $\perp_1$ and $\perp_2$ denote projections on two orthogonal directions in the plane perpendicular to the nematic director with the projection $\perp_1$ aligned along the scattering direction. For the averages in equation (13) we obtain

$$\sum_{i,j=1}^{N} \overline{(\mathbf{r}_i - \mathbf{r}_j)_{\alpha}^2} \cong b_{\alpha}^2 \frac{N^3}{3}, \quad \alpha = \parallel, \perp_1, \perp_2, \tag{14}$$

where $N \gg 1$. Using this result the expression for the scattering cross-section (13) becomes

$$\sigma \sim 1 - [(\mathbf{Q} - \mathbf{Q}_0)_{\parallel}^2 R_{\parallel}^2 + (\mathbf{Q} - \mathbf{Q}_0)_{\perp_1}^2 R_{\perp}^2 + (\mathbf{Q} - \mathbf{Q}_0)_{\perp_2}^2 R_{\perp}^2], \tag{15}$$

where $R_{\parallel}^2$ and $R_{\perp}^2$ are the mean projections of the radius of gyration of the anisotropic coil in the directions parallel and perpendicular to the nematic director, and

$$R_{\parallel}^2 = \frac{b_{\parallel}^2 N}{6}, \quad R_{\perp}^2 = \frac{b_{\perp}^2 N}{6}. \tag{16}$$

Notice that

$$\mathbf{Q} - \mathbf{Q}_0 = \mathbf{x} \tag{17}$$

is the neutron wave scattering vector.

In our reference frame $\mathbf{Q}_0$ is directed along the $\perp_1$ axis, i.e.

$$|\mathbf{Q}_0| = \mathbf{Q}_{0\perp_1} \equiv Q_0 \tag{18}$$

In spherical polar coordinates the scattering cross-section will be

$$\sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} \left( R_\parallel^2 \cos^2 \frac{\theta}{2} \cos^2 \phi + R_\perp^2 \cos^2 \frac{\theta}{2} \sin^2 \phi + R_\perp^2 \sin^2 \frac{\theta}{2} \right), \quad (19)$$

where $\theta$ is the scattering angle and $\phi$ is the azimuthal angle determined from the nematic director.

The case when $R_\parallel = R_\perp = R$ correponds to isotropic scattering, and the scattering cross-secton is well known:

$$\sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} R^2,$$

$$= 1 - \frac{4Q_0^2 \sin \theta/2}{3} R_g^2. \quad (20)$$

The small-angle approximation simplifies the scattering cross-section to

$$\sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} (R_\parallel^2 \cos^2 \phi + R_\perp^2 \sin^2 \phi). \quad (21)$$

A common and complete treatment of scattering from objects with azimuthal symmetry is given by Summerfield and Mildner [16]. Our consideration of a particular case of the problem, namely the anisotropic polymer coil, resembles the traditional one [17]. By changing variables in equation (21) we obtain

$$\sigma \sim 1 - 4Q_0^2 \frac{R_\parallel^2 R_\perp^2}{z_0^2} \left( \frac{x_\parallel^2}{R_\perp^2} + \frac{x_\perp^2}{R_\parallel^2} \right), \quad (22)$$

where $z_0$ is the distance between the sample and the detector while $x_\parallel$ and $x_\perp$ are cartesian coordinates in the detector plane. The curves of equal intensity obtained with equation (22) are ellipses in the detector plane; these have been observed by Kirste and Ohm [9].

## 5. Evaluation of the parameter $S^f$

The quantity $S^c$ can be defined in the framework of the model of a comb-like freely jointed chain, if the anisotropic parameter $a$ is known from experiment, by means of equations (16), (11), (9) and (8):

$$a^2 = \frac{R_\perp^2}{R_\parallel} = \frac{b_\perp^2}{b_\parallel^2} = \frac{(\mathbf{e}_\perp^c)^2}{(\mathbf{e}_\parallel^c)^2} = \frac{1 - S^c}{1 + 2S^c}, \quad (23)$$

or

$$S^c = \frac{1 - a^2}{1 + 2a^2}. \quad (24)$$

For values of the anisotropic parameter $a = 1 \cdot 25$ found by Kirste and Ohm [9], and $a = 1 \cdot 1$ found by Keller *et al.* [10], we find, respectively,

$$S^c(1\cdot25) \simeq -1/8, \quad S^c(1\cdot1) = -1/12. \quad (25)$$

Once the nematic order parameter $S^n$ is known, $S^f$ can be found by using equation (6). For example, if $S^n$ were $0\cdot5$ then we would have for $S^f$

$$S^f(1\cdot25) = -1/4 \text{ and } S^f(1\cdot1) = -1/6. \quad (26)$$

Note that if the mesogenic units are strictly perpendicular to the segments of the chain, then $S_m^f = -1/2$. A better characteristic is the relative order parameter which takes the values

$$S_r^f(1\cdot25) = S^f/S_m^f = 1/2, \quad S_r^f(1\cdot1) = 1/3. \tag{27}$$

In general only the second moment of the distribution function can be determined from experiment. In spite of this, we choose for illustration, the following one-parameter distribution:

$$f(\cos\gamma) = \tfrac{1}{2}\exp(-\mu^2\cos^2\gamma). \tag{28}$$

The constant in front of the exponential is taken so that when $\mu = 0$,

$$z_\mu = \frac{1}{2}\int_0^\pi \exp(-\mu^2\cos^2\gamma)\sin\gamma\,d\gamma \tag{29}$$

is equal to 1. Using equations (28) and (29) we have

$$\overline{\cos^2\gamma} = \frac{1}{2}\int_0^\pi f(\cos\gamma)\cos^2\gamma\sin\gamma\,d\gamma/z_\mu,$$

$$= \frac{1}{2\mu^2}\left[1 - \frac{2\mu\exp(-\mu^2)}{\sqrt{\pi}\phi(\mu)}\right], \tag{30}$$

where

$$\phi(\mu) = \frac{2}{\sqrt{\pi}}\int_0^\mu \exp(-t^2)\,dt$$

is the error function, and for the order parameter

$$S^f = \frac{1}{2}\left[\frac{3}{2\mu^2}\left(1 - \frac{2\mu\exp(-\mu^2)}{\sqrt{\pi}\phi(\mu)}\right) - 1\right]. \tag{31}$$

Then for values of the anisotropic parameter $1\cdot25$ and $1\cdot1$ and with the assumption of $S'' = 0\cdot5$, we find

$$\mu(1\cdot25) = 1\cdot65 \quad \text{and} \quad \mu(1\cdot1) = 1\cdot21 \tag{32}$$

from equations (26) and (31).

The contribution to the entropy of the system from the distribution $f(\cos\gamma)$ can be estimated from

$$S = -k\frac{1}{z_\mu}\int_0^\pi f\ln(2f/z_\mu)\sin\gamma\,d\gamma, \tag{33}$$

where $k$ is the Boltzmann constant. In the accepted normalization for $z_\mu$ (see equation (29)) $S$ is less than zero. For values of $\mu$ from equation (32) we have

$$S(1\cdot25) = -0\cdot203k \quad \text{and} \quad S(1\cdot1) = -0\cdot076k. \tag{34}$$

For the free energy, $F = -TS$, we have, at 400 K,

$$F(1\cdot25) = 163\,\text{cal/mol} \quad \text{and} \quad F(1\cdot1) = 61\cdot19\,\text{cal/mol}. \tag{35}$$

Note that at the phase transition from the isotropic to the nematic phases the entropy is discontinuous because the distribution is also discontinuous. If we denote the distribution in the isotropic phases by $f_p$, then the entropic change will be

$$\Delta S = S_f - S_{f_p}. \tag{36}$$

Thus, in addition to the well-known entropy change due to the distribution $g$, we find a jump due to the distribution $f$ and given by (36).

We now consider one defect of the comb-like freely jointed chain model. Immediately from equations (2), (8) and (9) we notice that the radius of gyration of the macromolecule is not changed at the transition from the isotropic to the nematic phase;

$$R_g^2 = \frac{Nb^2}{6} \left( \frac{1 + 2S^c}{3} + 2\frac{1 - S^c}{3} \right),$$

$$= \frac{Nb^2}{6}. \tag{37}$$

In contrast, experiment reveals that the radius of gyration increases at the transition. It can be shown that the correlation between the segments of the chain causes this increase. However in the model considered here these correlations are absent, and consequently the radius of gyration remains the same. However, the experimentally-measured increase of the radius of gyration is very small, and therefore our estimate of the parameter $S^f$ is reasonable.

## 6. Conclusions

Analysis of the anisotropy of the comb-like liquid-crystalline polymer's macromolecule coil in the nematic phase shows that it results from the correlation between the orientations of the mesogenic units and segments of the backbone. The experimental data reveal that the mesogens tend to become perpendicular to the backbone segments. The connection between the anisotropy parameter $a$, the nematic order parameter, and the parameter $S^f$ (see equations (6) and (24)) is established in the framework of a simple model. Consequently, if we have data on the order parameter in the nematic phase and the anisotropy parameter, then $S^f$ can be estimated, which is equivalent to finding the second moment of the distribution of the mesogenic units relative to the backbone segments.

For the experimentally-measured values $a = 1 \cdot 1$, $1 \cdot 25$ and an estimate for $S^n$ of $0 \cdot 5$, the parameters $S^f$, reduced to the minimum of $-1/2$, equal $1/3$ and $1/2$, respectively. The results of this work show that measurement of the mean square of the projections of radius of gyration of the anisotropic coil in the nematic phase by the method of small-angle neutron scattering provides information on the orientational correlations between the mesogenic units and segments of the main backbone.

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