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**COMB-LIKE
MACROMOLECULE CONFORMATION
IN NEMATIC PHASE.
THE SMALL-ANGLE NEUTRON SCATTERING
DATA INTERPRETATION**

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At the present time a growing interest is observed to the study of the liquid-crystalline state of polymers. Comb-like polymers with mesogenic molecules represent a large class of polymers displaying liquid-crystalline (LC) properties. There is extensive information on the properties of such polymers in dilute solutions as well as in the block^{/1-6/}.

The studies of LC polymers with mesogenic molecules in the block were performed by various methods, such as X-ray scattering and diffraction, NMR-spectroscopy, optical diffraction and others. Measurements mainly concerned the ordering of mesogenic molecules and structure changes in phase transitions^{/1-6/}. However, the conformation of the main macromolecular chain was not studied.

The labelling method allows one to extract direct information on the conformation of a single macromolecule in the block from the neutron scattering data^{/7,8/}.

Recent experiments based on the small angle scattering and neutron diffraction have clarified the conformation of the main chain of the macromolecule in mesophases^{/9,10/}. The radii of gyration of the main chain parallel $R_{||}$ and perpendicular R_{\perp} to the axis of orientation given in^{/9/} are $9,4 \pm 0,5$ nm and $11,8 \pm 0,6$ nm respectively. For the anisotropy parameter the authors obtained

$$a = \frac{R_{\perp}}{R_{||}} = 1,25. \quad (1)$$

The mean square radius of gyration for the macromolecular coil of the main chain

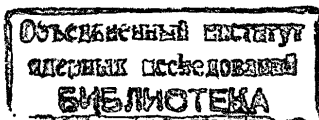
$$R^2 = \frac{R_{||}^2 + 2R_{\perp}^2}{3} \quad (2)$$

is the same in isotropic and nematic phases.

It is known that in LC comb-like polymers the rigidity of the main chain increases. The Kuhn segment of such a macromolecule equals 3.0 nm and includes 24 monomers.

Numerous experiments show that there is an intramolecular ordering in mesogenic molecules^{/2,4/}.

Though mesogenes have a flexible joint with the main chain, the influence of the intramolecular ordering on the flexibility is observed. The experimental results can be explained by anisotropy of local rigidity.



As is known, the mesogenic molecules with intramolecular ordering are mainly arranged on the plane. Evidently, the rigidity of the macromolecule in this plane must be greater than the one directed towards the normal to this plane. It is also obvious that in the isotropic phase the normal direction to this plane will change along the chain. Therefore the anisotropy of rigidity for the whole macromolecule doesn't exist. It can be only local (fig. 1).

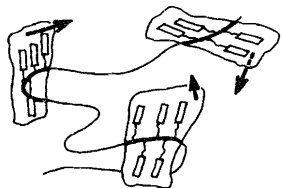


Fig.1
The macromolecule in the isotropic phase. The side mesogenic groups have arbitrary orientations, hence, the anisotropy of rigidity is local.

Now let us try to explain the results of experiments by means of the anisotropy of rigidity. Suppose that in the nematic phase the intramolecular order is not broken along the whole chain, while the anisotropy of rigidity has constant direction due to the interaction with the nematic field. The rigidity will be greater along the nematic director (fig. 2).

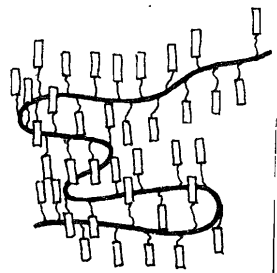


Fig.2.
The macromolecule in the nematic phase. Side mesogenic groups are oriented along the chain. The macroscopic ordering of the mesogenes results in the appearance of macroscopic anisotropy of the rigidity.

Under this assumption the distribution function for distances between the i and j monomers in the Gaussian approximation is

$$G(\vec{r}_i - \vec{r}_j) = \frac{1}{(2\pi|i-j|b_{\parallel}^2)^{1/2}} \frac{1}{2\pi|i-j|b_{\perp}^2} e^{-\frac{(r_{i\parallel} - r_{j\parallel})^2}{2|i-j|b_{\parallel}^2}} e^{-\frac{(\vec{r}_{i\perp} - \vec{r}_{j\perp})^2}{2|i-j|b_{\perp}^2}} \quad (3)$$

This distribution differs from the well-known function by the fact that here the projections of the Kuhn segment are not equal. Using (3) one can calculate the following averages:

$$\overline{(r_{i\parallel} - r_{j\parallel})^2} = b_{\parallel}^2 |i-j| \quad (4)$$

$$\overline{(r_{i\perp} - r_{j\perp})^2} = 2b_{\perp}^2 |i-j| \quad (5)$$

$$\overline{(\vec{r}_i - \vec{r}_j)^2} = (b_{\parallel}^2 + 2b_{\perp}^2) |i-j| \equiv b^2 |i-j|. \quad (6)$$

From (4) and (5) we find the radii of gyration for the anisotropy coil in the directions parallel and perpendicular to the direction of orientation. Their ratio

$$\frac{R_{\perp}}{R_{\parallel}} = \frac{b_{\perp}}{b_{\parallel}} \quad (7)$$

determines the anisotropy a of the polymer coil. Since the rigidity of the molecule in the parallel direction is greater than that in the perpendicular direction, we have

$$b_{\parallel} > b_{\perp} \quad (8)$$

and $a < 1$, which is in conflict with experimental data.

Therefore, our assumption that the intramolecular ordering is not broken along the whole chain is not true. Probably, the intramolecular order is broken as a result of the interactions of mesogenic groups belonging to different macromolecules. Similar intramolecular interactions leading to the broken intramolecular ordering have been observed in [11,4].

Now suppose that in parallel segments of the macromolecule chain the intramolecular order is upset while it remains unchanged at the segments of the chain perpendicular to the nematic director (fig. 3).

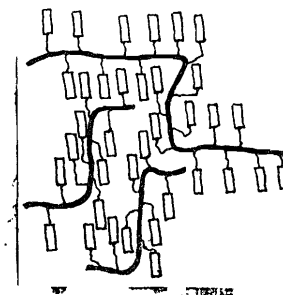


Fig.3.
The conformation of the macromolecule corresponding to the proposed mode. There are parts of the chain with intramolecular ordering (they are perpendicular to the axis of nematic director) and parts with broken orientation (they are parallel to the nematic director).

It is obvious that such segments with broken ordering are energetically less beneficial. Taking it into account the distribution function for two monomers separated by one Kuhn segment can be written as follows

$$G(\vec{r}_i - \vec{r}_{i-1}) \sim e^{-\frac{(\vec{r}_i - \vec{r}_{i-1})^2}{2b_L^2}} e^{-\frac{U(\vec{n}(\vec{r}_i - \vec{r}_{i-1}))^2}{kT|\vec{r}_i - \vec{r}_{i-1}|^2}} \quad (9)$$

The first term in (9) describes the isotropic distribution with the projection b_L of the Kuhn segment on an arbitrary direction. The second term is the Boltzmann factor. Here k is the Boltzmann constant, T is the temperature, U is a positive constant with the energy dimension and \vec{n} is the nematic director. The Boltzmann factor makes the statistical weight of the segments placed along the direction of orientation less than for the segments placed perpendicular.

Using the approximation

$$(\vec{r}_i - \vec{r}_{i-1})^2 \approx \overline{(\vec{r}_i - \vec{r}_{i-1})^2} = 3b_L^2 \quad (10)$$

we simplify (9) as follows:

$$G(\vec{r}_i - \vec{r}_{i-1}) \sim e^{-\frac{(r_{i\parallel} - r_{i-1\parallel})^2}{2b_{\parallel}^2}} e^{-\frac{(r_{i\perp} - r_{i-1\perp})^2}{2b_{\perp}^2}}, \quad (11)$$

where

$$b_{\parallel}^2 = \frac{b_L^2}{1 + \frac{2U}{3kT}} \quad (12)$$

Using (11) we can obtain the distribution function for any i and j of type (3).

From (12) U can be estimated using the experimentally obtained anisotropy quantity (1). For a room temperature

$$U \approx 500 \text{ kal/mol} \quad (13)$$

The energy U is the difference between the energy of one mole of Kuhn segments oriented along the nematic direction and those oriented perpendicular. Assuming that the Kuhn segment contains 24 mesogenes we obtain the energy for one mole of mesogenic groups

$$U_1 \approx 20 \text{ kal/mol} \quad (14)$$

The energy U_1 is the difference between the energy of a mode of mesogenic side groups in the segments of the chain with intramolecular ordering and the segments with broken order. (All the above considerations concern the nematic phase).

Let us find the cross section of neutron scattering on the anisotropy coil with the distribution function (3). It is well known that the cross section of the elastic coherent scattering for one macromolecule is

$$\sigma \sim \sum_{i,j=1}^N e^{i(\vec{Q} - \vec{Q}_0)(\vec{r}_i - \vec{r}_j)}; \quad |\vec{Q}| = |\vec{Q}_0|, \quad (15)$$

where \vec{Q}_0 and \vec{Q} are the wave vectors for incident and scattered neutrons, respectively.

Expanding the exponential function into a series, under the small-angle assumption and considering the first terms, we obtain

$$\sigma \sim N^2 \left\{ 1 - \frac{1}{2N} \sum_{i,j=1}^N \left[(\vec{Q} - \vec{Q}_0)_{\parallel}^2 \overline{(\vec{r}_i - \vec{r}_j)_{\parallel}^2} + (\vec{Q} - \vec{Q}_0)_{\perp 1}^2 \overline{(\vec{r}_i - \vec{r}_j)_{\perp 1}^2} + (\vec{Q} - \vec{Q}_0)_{\perp 2}^2 \overline{(\vec{r}_i - \vec{r}_j)_{\perp 2}^2} \right] \right\} \quad (16)$$

Indices \parallel and \perp denote projections on two orthogonal directions on the plane perpendicular to the axis of nematic orientation with the projection $\perp 1$ aligned along the scattering direction. For the averages in (16) we obtain

$$\sum_{i,j=1}^N \overline{(\vec{r}_i - \vec{r}_j)_{\parallel}^2} \approx b_{\parallel}^2 \frac{N^3}{3}; \quad N \gg 1$$

$$\sum_{i,j=1}^N \overline{(\vec{r}_i - \vec{r}_j)_{\perp 2}^2} \approx b_{\perp}^2 \frac{N^3}{3} \quad (17)$$

The expression for the scattering cross section (16) with account of (17) becomes

$$\sigma \sim 1 - \left\{ (\vec{Q} - \vec{Q}_0)_{\parallel}^2 R_{\parallel}^2 + (\vec{Q} - \vec{Q}_0)_{\perp 1}^2 R_{\perp}^2 + (\vec{Q} - \vec{Q}_0)_{\perp 2}^2 R_{\perp}^2 \right\}, \quad (18)$$

where R_{\parallel} and R_{\perp} are the radii of gyration of the anisotropic coil in the directions parallel and perpendicular to the axis of nematic ordering and

$$R_{\parallel}^2 = \frac{B_{\parallel}^2 N}{6} ; R_{\perp}^2 = \frac{B_{\perp}^2 N}{6} . \quad (19)$$

Notice that

$$\vec{Q} - \vec{Q}_0 = \vec{\alpha} \quad (20)$$

is the neutron wave scattering vector.

In our frame of reference \vec{Q}_0 is directed along the $\perp 1$ -axis, i.e.,

$$|\vec{Q}_0| = Q_{0\perp 1} = Q_0 . \quad (21)$$

In spherical coordinates the scattering cross section will be

$$\begin{aligned} \sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} (R_{\parallel}^2 \cos^2 \frac{\theta}{2} \cos^2 \varphi + R_{\perp}^2 \cos^2 \frac{\theta}{2} \sin^2 \varphi + \\ + R_{\perp}^2 \sin^2 \frac{\theta}{2}) , \end{aligned} \quad (22)$$

where θ is the scattering angle, φ is the azimuthal angle reckoned from the axis of nematic ordering.

The case when $R_{\parallel} = R_{\perp}$ corresponds to isotropic scattering, and the scattering cross section is well known

$$\sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} R_{\perp}^2 . \quad (23)$$

The small-angle approximation simplifies the scattering cross section to

$$\sigma \sim 1 - 4Q_0^2 \sin^2 \frac{\theta}{2} (R_{\parallel}^2 \cos^2 \varphi + R_{\perp}^2 \sin^2 \varphi) . \quad (24)$$

Evidently, for the cross section (24) the Zimm procedure gives different radii of gyration for different directions. By changing variables in (24) we obtain

$$\sigma \sim 1 - 4Q_0 \frac{R_{\perp}^2 R_{\parallel}^2}{Z_0} \left(\frac{x_{\parallel}^2}{R_{\perp}^2} + \frac{x_{\perp}^2}{R_{\parallel}^2} \right) , \quad (25)$$

where Z_0 is the distance between the sample and detector and x_{\parallel} and x_{\perp} are the Cartesian coordinates in the detector plane.

The curves of equal intensity obtained with (25) are ellipses in the detector plane.

Now we will summarize the results of this paper.

The model in which the intramolecular ordering is not broken only in segments oriented perpendicular to the nematic director enabled us to explain the anisotropy of the macromolecular coil observed in experiment. Small anisotropy of the coil allowed us to consider this model in the framework of the Gaussian chain with different Kuhn-segment projections.

On the basis of the proposed model and experimental data we estimated the energy of the intramolecular ordering for one mesogenic side group to be 20 cal/mol.

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Конформация гребнеобразной макромолекулы в нематической фазе
Интерпретация данных малоуглового рассеяния нейтронов

Предложена структурная модель гребнеобразной макромолекулы в нематической фазе, согласно которой помимо участков цепи с внутримолекулярным упорядочением существуют участки, в которых такое упорядочение нарушено. Эта модель согласуется с последними данными малоуглового рассеяния нейтронов на ориентированных жидкокристаллических полимерах. Дана оценка разности энергии между боковыми мезогенными группами, находящимися в участках указанных типов.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Comb-Like Macromolecule Conformation in Nematic Phase.
The Small-Angle Neutron Scattering Data Interpretation

The structure model of a comb-like macromolecule in the nematic phase is proposed. According to this model the main chain of the macromolecule includes segments with intramolecular order as well as those with the broken order. This model is in good agreement with recent data on the small angle neutron scattering on oriented liquid-crystalline polymers. An estimate of the energy difference between side mesogenic groups in these segments is given.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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