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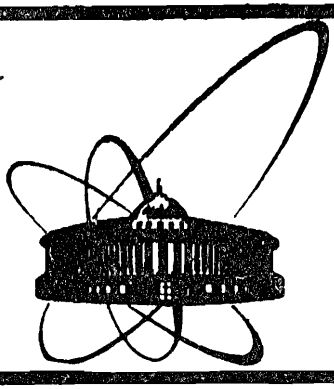

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COMB-LIKE MACROMOLECULE CONFORMATION IN SMECTIC PHASE.

Interpretation of Neutron-Scattering Data

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At present the growing interest is observed to the study of the liquid-crystalline (LC) state of polymers in different mesophases [1-3]. The method of selected deuteration allows one to obtain direct information of the structure of the conformation of the macromolecule in the block from the neutron scattering data.

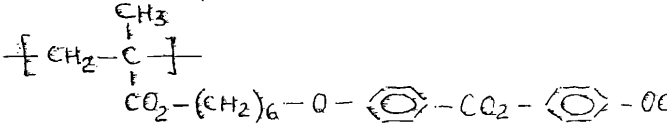
First measurements of the projections of the radius of gyration of the main chain of the comb-like macromolecule in the nematic and smectic mesophases performed by the small angle neutron scattering technique (SANS) are presented in [4,5].

In [6] the interpretation of the neutron scattering data for the LC polymer in the nematic phase is given.

This paper deals with the interpretation of presently available data on neutron scattering on the smectic polymer from [5].

1. Experimental data [5]

In the paper [5] by SANS and the neutron diffraction (ND) methods the comb-like LC polymer has been investigated with the chain of the type



with the molecular weight $3 \cdot 10^5$ Dalton.

The macromolecule of such polymer contains 680 monomers and has the contour length 1700 Å.

Measured values of the projections of the radius of gyration for the macromolecule in the smectic phase are

$$R_x = 21 \pm 3\ \text{Å}\ ;\ R_y = 86 \pm 9\ \text{Å}, \quad (1)$$

where R_x and R_y are the projections of the radius of gyration on the directions perpendicular (x) and parallel (y) to the smectic layer plane.

The total radius of gyration of the macromolecule in the smectic phase can be expressed by projections:

$$R_S \equiv \left(R_x^2 + 2R_y^2\right)^{1/2}. \quad (2)$$

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The measured value of the radius of gyration in the isotropic phase

$$R_I = 105\,\text{Å}. \qquad (3)$$

The comparison between (2) and (3) shows that the rigidity of the macromolecule in the smectic phase is greater than in the isotropic phase.

The thickness of the smectic layer D is measured by the ND method

$$D = 29{,}5\,\text{Å}. \qquad (4)$$

Besides the peak corresponding to the interplane distance, the diffractogram displays diffuse spots in the small angle region with a smoothed maximum which relates to the Bragg distances 56Å and 38Å along the x-axis and y-axis, respectively.

Interpreting these data the authors in /5/ suppose that the macromolecular chain locates in one smectic layer crossing it many times. Evidently, the proposed conformation is based on the very large anisotropy of the projections of the radius of gyration. However, the radius of gyration of the macromolecule is its integral characteristic, and therefore, different conformations with the same radius of gyration are possible. In the present paper it is supposed that the macromolecule has the conformation of anisotropic statistical coil with parameters determined on the basis of available experimental data.

2. The Model of Anisotropic Freely Joint Chain

The large anisotropy of the projections of the radius of gyration of the LC polymer macromolecular chain in the smectic phase is the result of the difficulties in crossing through the mesogenic layer. It is natural since the smectic phase can be considered as a microphase separation of mesogenics and alyphatic parts /7/.

Let us refer to the part of the chain intersecting the smectic layer as the crossing segment. It is reasonable to suppose that the crossing segment will straighten and so will be practically perpendicular to the smectic layer. The crossing segment forms a defect in the smectic layer on the molecular level. The detailed structure of this defect is unknown, though the SANS method as shown below allows one to evaluate the number of such defects.

Let us construct the model of freely joint chain with the following properties:

1. The chain performs random walks in the smectic layer plane

so that the backbone of the macromolecule is located in the alyphatic layer. Let us describe the flexibility of such a two-dimensional chain by the Kuhn segment $b_\perp$.

2. The chain performs random walks between the intermediate layers with the step equal to the inter layer thickness D.

3. Since the transition through the smectic layer is quite difficult, it must be accounted by introducing different probabilities for the steps of the freely joint chain in the plane and between the layers.

The simplest way to do it is to use the lattice model. In this case the space distribution function for one segment of the freely joint chain is

$$\begin{aligned} g(x,y,z) = {} & \frac{1}{2}\left[\delta(x-D)+\delta(x+D)\right]\delta(y)\,\delta(z)\,p + \\ & + \frac{1}{2}\left[\delta(y-b_\perp)+\delta(y+b_\perp)\right]\delta(x)\,\delta(z)\,\frac{1-p}{2} + \\ & + \frac{1}{2}\left[\delta(z-b_\perp)+\delta(z+b_\perp)\right]\delta(x)\,\delta(y)\,\frac{1-p}{2}, \end{aligned} \qquad (5)$$

where δ is the Dirac delta function and p is the normalized probability of the interlayer transition. If $p = 1/3$, then the step probability is equal for all three directions.

As is well known, the mean square distance between the ends of the freely joint chain is

$$\overline{h^2} = N\,\overline{(\vec{r})^2}, \qquad (6)$$

where N is the number of chain segments, $\vec{r}$ is the radius vector of one Kuhn segment and $\overline{(\vec{r})^2}$ is given by

$$\overline{(\vec{r})^2} = \int dx\,dy\,dz\; g(x,y,z)(x^2+y^2+z^2). \qquad (7)$$

Accounting (5) and (7) for the anisotropic chain we obtain

$$\overline{h^2} = N\left[2\,\frac{1-p}{2}\,b_\perp^2 + pD^2\right]. \qquad (8)$$

For the mean square projections of the distance between the ends of the chain we obtain

$$\overline{h_x^2} = N\cdot p\,D^2\,;\quad \overline{h_y^2} = N\,\frac{1-p}{2}\,b_\perp^2\,;\quad \overline{h_z^2} = N\,\frac{1-p}{2}\,b_\perp^2. \qquad (9)$$

It is well known that any real chain (without effects of excluded volume) can be approximated by equivalent freely joint chain which has the same contour length and the average distance between the ends as those of the real chain.

The quantity of the Kuhn segment A and their number N in the chain are defined as

$$\overline{h^2} = L A \quad ; \quad N = \frac{L}{A}, \tag{10}$$

where L is the contour length of the chain.

In the case when the chain is characterized by two segments $b_\perp$ and D, we find N from

$$L = \sum_{i=1}^{N} |\vec{r}_i| = N\overline{|r_i|}. \tag{11}$$

And using (5) and (7) we obtain

$$L = N[(1-\rho) b_\perp + \rho D]. \tag{12}$$

The radius of gyration depends on the distance between the ends of the chain as

$$R_g^2 = \frac{h^2}{6}. \tag{13}$$

Therefore, for the projections of the radius of gyration we have

$$R_x^2 = \frac{N}{6} \rho D^2, \tag{14}$$

$$R_y^2 = \frac{N}{6} \frac{(1-\rho)}{2} b_\perp^2. \tag{15}$$

In equations (12), (14) and (15) the quantities R_x, R_y and D are determined experimentally, the contour length L is the known quantity, and unknown quantities are the chain parameters N, $b_\perp$ and ρ.

It must be taken into account that the real chain performs random walks not strictly in the plane, but within the whole intermediate layer having a finite thickness.

These random walks will not affect R_x value because of the small thickness of the intermediate layer, but they must be accounted in the expression for the contour length (12).

Let us denote by ΔL_x the contour length of the chain located outside the plane. It is reasonable to suppose that

$$\Delta L_x = N(1-\rho)\Delta, \tag{16}$$

where Δ is the mean contour length per one Kuhn segment of the freely joint chain in the intermediate layer.

With (16) taken into account equation (12) becomes

$$L = N[(1-\rho)(b_\perp + \Delta) + \rho D], \tag{17}$$

Δ is unknown quantity. Let us suppose that it is of an order of the thickness of the intermediate layer (5–10Å).

For convenience introduce in equations (14), (15) and (17) the following notation:

$$N_\parallel = N\rho \; ; \; N_\perp = N - N_\parallel \; ; \; L_\parallel = N_\parallel D \; ; \; L_\perp = L - L_\parallel \tag{18}$$

then the equations become

$$R_x^2 = \frac{1}{6} N_\parallel D^2, \tag{19}$$

$$R_y^2 = \frac{1}{6} \frac{N_\perp}{2} b_\perp^2, \tag{20}$$

$$L_\perp = N_\perp (b_\perp + \Delta), \tag{21}$$

$N_\parallel$ and $N_\perp$ are average numbers of the chain segments oriented normally to the smectic layer and parallel to it, respectively. For the isotropic distribution

$$N_\parallel = \frac{N}{3} \quad ; \quad N_\perp = 2 \cdot \frac{N}{3}. \tag{22}$$

The quantities R_x and D are measured experimentally, therefore $N_\parallel$ can be defined from (19) as

$$N_\parallel = \frac{6R_x^2}{D^2} \tag{23}$$

$N_\parallel$ that is the number of crossing segments (defects) for one macromoleoular chain. The quantity

$$k = \frac{L_\parallel}{L} = \frac{6R_x^2}{D \cdot L} \tag{24}$$

is a characteristic of the smectic phase.

Now let us estimate the accuracy of the quantity k. Expression (24) is obtained under the assumption that the crossing segment is stretched as far as possible, i.e., it has transconformation. Another inaccuracy in (24) reflects the indefinite thickness of intermediate and mesogenic layers. Nevertheless, all this does not influence the quantity $N_\parallel$.

Using equations (20) and (21) we define

$$b_\perp = b_\perp^\circ \left[1 + \left(\frac{\Delta}{b_\perp^\circ}\right) - \left(\frac{\Delta}{b_\perp^\circ}\right)^2\right], \qquad (25)$$

$$N_\perp = \frac{L_\perp}{L}\left[1 - 2\left(\frac{\Delta}{b_\perp^\circ}\right) + 5\left(\frac{\Delta}{b_\perp^\circ}\right)^2\right], \qquad (26)$$

where

$$b_\perp^\circ = \frac{12\,R_y^2}{L_\perp} \qquad (27)$$

The quantities $b_\perp$ and $N_\perp$ are defined with an accuracy of the second order of the parameter $\Delta / b_\perp^\circ$. At last, let us express p in terms of new variables:

$$p = \frac{N_\parallel}{N_\parallel + N_\perp}. \qquad (28)$$

3. Calculation of the Parameters for the Model Chain

Using experimental data from /5/ and (23) we obtain

$$N_\parallel = 3,04. \qquad (29)$$

It is the number of crossing segments accounted for one macromolecular chain of the polymer with a given molecular weight. From (24) we obtain for k :

$$k = 0,06 \qquad (30)$$

that is, crossing segment amount to approximately 6% of the whole chain length.

$N_\parallel$ crossing segments divide the chain into $N_\parallel + 1$ quasi-two-dimensional subcoils. The typical conformation of the macromolecular chain of the smectic LC polymer is shown in Fig.1.

The mean square distance between the ends of such a subcoil $\overline{(h_y^1)^2}$ is independent of its internal structure and we can write

$$R_y^2 = \frac{(N_\parallel + 1)\,\overline{(h_y^1)^2}}{6}, \qquad (31)$$

where R_y is the experimentally measured projection of the radius of gyration for the whole coil. Using (31) and from (1) we obtain

$$h_y^1 = 105\ \text{Å}. \qquad (32)$$

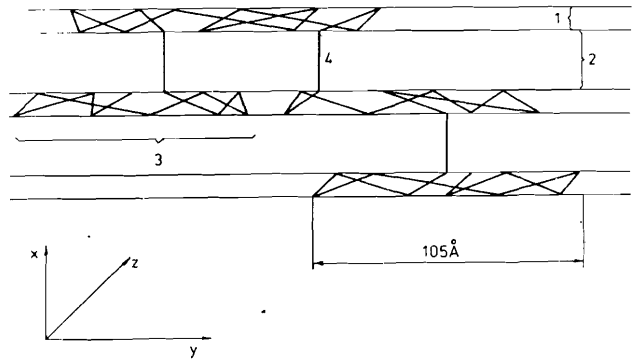

Fig.1. Typical conformation of the macromolecules backbone. Quasi-two-dimensional subcoils 3 placed in the intermediate layer 1, are connected with crossing segments 4. These segments create defects in the mesogenic layer 2. Experimental date are taken from /5/ .

Correspondingly, for the projection of the radius of gyration and the chain length of one subcoil we obtain

$$R_y = 43\,\text{Å}\ ; \quad L_\perp^1 = 400\,\text{Å}, \qquad (33)$$

where $L_\perp^1$ is the average length of the subcoil chain. (In general, for the real subcoil h_y^1 and $L_\perp^1$ largely variate since crossing segments appear occasionally). Note that the quantities in (32) and (33) are independent of the uncertainty in Δ , while $b_\perp$, N and p as seen from (25); (26) and (28) depend on Δ . These quantities for two values of Δ are:

$b_\perp^\circ = 55.1$ Å ; $N_\perp^\circ = 29.2$; $p^\circ = 0.094$ for $\Delta = 0$ (34)

$b_\perp = 63$ Å ; $N_\perp = 23.4$; $p = 0.114$ for $\Delta = 10$ Å. (35)

As is seen from (34) and (35), values of $b_\perp$, N and p are rather weakly dependent on the parameter Δ .

Let us take the quantity $b_\perp = 60$ Å . The comparison between $b_\perp$ and the Kuhn segment for the coil in the isotropic phase (39 Å) points out the considerable increase of the chain rigidity of the two-dimensional subcoil. It is caused primarily by the decreasing number of goshisomers in quasi-two-dimensional chain and by effects of excluded volume appearing in this case /8/ . In the three-dimensional case according to the Flory theorem the chain behaves as an ideal one and effects of excluded volume can be neglected.

From all the above, it follows that it is desirable to measure the Kuhn segment directly by the Kratky technique [9]. Measuring only R_y is not sufficient for a precise definition of $b_\perp$ because of uncertainty in Δ and the influence of excuded volume effects.

4. Average Distance between Defects

Let us estimate the average distance between the crossing segments in one smectic layer using

$$r_y \simeq \left(\frac{M}{N_A \, n \, D \, N_{||}} \right)^{1/2} \qquad (36)$$

which can be obtained from simple considerations. Here r_y is the projection of the distance between defects on the y-axis, M is the polymer molecular weight, N_A is the Avogadro number and n is the polymer density. Assuming $n \approx 1$ g·cm^{-3} and taking D and $N_{||}$ from (4) and (29) we obtain

$$r_y \approx 74 \text{ Å}. \qquad (37)$$

It is easy to show that the average distance between the projections of two crossing segments located in different smectic layers will be twice as small, i.e., 37 Å. It can be assumed that the small angle peak in diffractogram in [5] which relates to Bragg distances 56 Å and 38 Å in directions x and y, respectively, results from the scattering on defects located in different smectic layers (Fig. 2).

5. Temperature Effects

Studies of the temperature dependence of the projections of the macromolecule main chain radius of gyration can give information on the nature of defects of smectic comb-like LC polymers.

Suppose that the smectic phase is in equilibrium state, i.e., there is a dynamical balance in processes of the appearance and disappearance of smectic defects at the given temperature. In this case the probability of defect appearance p can be written as follows

$$p = \frac{e^{-\frac{\Delta F}{RT}}}{2 + e^{-\frac{\Delta F}{RT}}}, \qquad (38)$$

where R is the molar gas constant, T is the temperature and $e^{-\Delta F/RT}$ is the statistical weight of appearance of the crossing segment. Estimating with (38) the energy of smectic defect E ($\Delta F \sim E$)

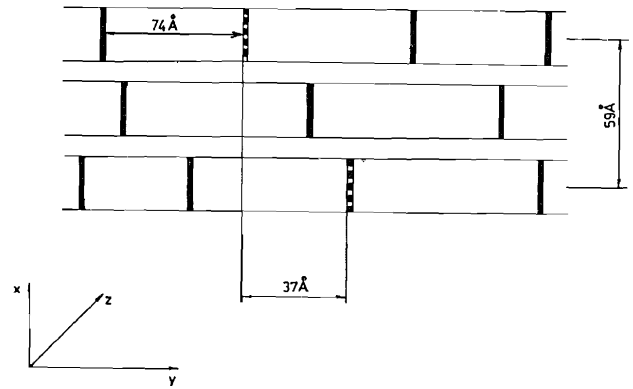

Fig. 2. Crossing segments in the smectic phase. Average distance between projections is 74Å. The Bragg distance measured in [5] is equal to the distance between marked segments.

at $T = 330^\circ$K for $p = 0.01$ obtained in (34) we have

$$E \approx 1000 \text{ cal/mole}. \qquad (39)$$

The temperature dependence of p (with known E) is

$$p \approx p_0 \, e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \qquad (40)$$

and using (14) we obtain the temperature dependence of R_x

$$R_x(T) = R_x(T_0) \, e^{-\frac{E}{2R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}. \qquad (41)$$

The considered polymer is in smectic phase in the temperature range from 45°C to 110°C. For this temperature difference we obtain using (41)

$$\frac{R_x(T_{max}) - R_x(T_{min})}{R_x(T_{min})} \approx 0{,}1. \qquad (42)$$

Thus the equilibrium theory predicts the increase of R_x by 10% in the smectic temperature range.

Note that the defect energy E is composed of the energy of

segregation of mesogens and alyphatic parts of the macromolecule and the energy of the main-chain binding.

6. Conclusions

According to assumptions of the present paper random walks of a polymer chain can be divided into two types - random walks in the smectic layer and those between layers. In the latter case the step of random walks equals to the thickness of the smectic layer. Therefore, measuring the projection of the radius of gyration of the macromolecule in the direction α (Fig.1) and using (23) one can determine the number of crossing segments (defects) $N_{\parallel}$.

The crossing segments divide the macromolecular chain into quasi--two-dimensional parts with the conformation of statistical coil. The average size of these subooils can be defined using (31) and measuring the projection of the radius of gyration in the y-direction.

The absence of data on the influence of excluded volume effects and, besides, the random walks of the main chain in the x-direction in the range of the intermediate sublayer prevent a precise definition of the Kuhn segment $b_{\perp}$ in the plane. Therefore, it is desirable to measure the Kuhn segment (or the persistence length) directly in the smectic layer plane by the Kratky technique.

We hope that the use of the small-angle neutron scattering and the neutron diffraction techniques along with other methods (X -ray diffraction, NMR etc) will soon give a complete presentation of the cob-like LC polymer structure.

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E17-86-287

Конформация гребнеобразной макромолекулы в смектической фазе; интерпретация данных нейтронного рассеяния

Простое теоретическое рассмотрение позволяет определить конформацию центрального хребта макромолекулы по данным нейтронного эксперимента. Макромолекулярная цепь в смектической фазе разделяется на квазидвумерные клубки, расположенные случайным образом в различных смектических слоях. Размеры клубков не зависят от молекулярного веса полимера. Двумерные субклубки связаны между собой небольшим количеством переходов. Их можно рассматривать как дефекты смектической фазы. Измерение радиуса инерции макромолекулы в смектической фазе с помощью метода малоуглового рассеяния нейтронов позволяет с помощью предложенной модели определить количество дефектов.

Работа выполнена в Лаборатории теоретической физики ОИЯИ

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Comb-Like Macromolecule Conformation in Smectic Phase. Interpretation of Neutron-Scattering Data

Simple theoretical consideration allows one to define the conformation of the macromolecule main chain from the neutron experiment data. The macromolecular chain in the smectic phase is divided into quasi-two-dimensional coils randomly placed in different smectic layers. The size of these coils is independent of the polymer molecular weight. The two-dimensional subcoils are connected with each other by a number of transitions. They can be considered as defects of the smectic phase. The proposed model allows one to define the number of defects measuring the radius of gyration of the smectic macromolecule by the small angle neutron scattering technique.

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

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