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## Liquid Crystals

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### Thermotropic liquid-crystalline polymers XXIII. Peculiarities of uniaxial orientation of comb-like liquid-crystalline polymers under mechanical stress

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## Thermotropic liquid-crystalline polymers

### XXIII†. Peculiarities of uniaxial orientation of comb-like liquid-crystalline polymers under mechanical stress

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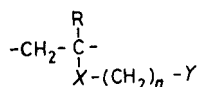
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The structure of oriented samples of liquid-crystalline side-chain polymers has been studied by X-ray diffraction. The arrangement of the different fragments of the macromolecules is shown to be dependent on the mesophase type of the initial melt. The orientation of the nematic melt leads to parallel alignment of mesogenic groups along the fibre axis. In the smectic melt, the smectic layers are arranged along the fibre axis with the mesogenic groups normal ( $S_A$  and  $S_B$ ) or tilted ( $S_C$  and  $S_F$ ) to it.

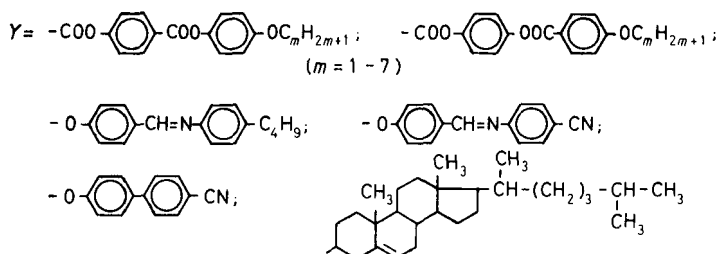
#### 1. Introduction

The type of mesophase in liquid-crystalline side-chain polymers can be identified by the X-ray analysis of oriented fibres [1]. However the arrangement of the different fragments of the macromolecules in uniaxially oriented samples is not yet elucidated. Some new data have been discussed [2-8] but the limited number of polymers studied does not allow definite conclusions to be reached. It is necessary to note that in the papers [3-6] the structure of liquid-crystalline polymers oriented only by a magnetic field was studied. In this case the mesogenic groups are always arranged in the direction of the field applied. No special attention was given to the structure of liquid-crystalline polymers formed by drawing fibres from mesomorphic melts. Indeed, in this case the joint role of the main chain and the mesogenic groups defining the mesophase type should be essential.

Therefore in this paper we present the results of X-ray studies of a wide range of liquid-crystalline side-chain polymers



where R = H or CH<sub>3</sub>; X = COO or CONH; n = 2 - 14



†Part XXII. FREIDZON, YA. S., BOIKO, N. I., SHIBAEV, V. P., and PLATÉ, N. A., 1986, *Eur. Polym. J.*, **22**, 13.

uniaxially oriented under mechanical stress. The synthesis of these polymers, their mesophase types, thermal properties and some structural data are described elsewhere [7–14]. Here we stress some general features of the orientation of liquid-crystalline polymers in the nematic and smectic phases.

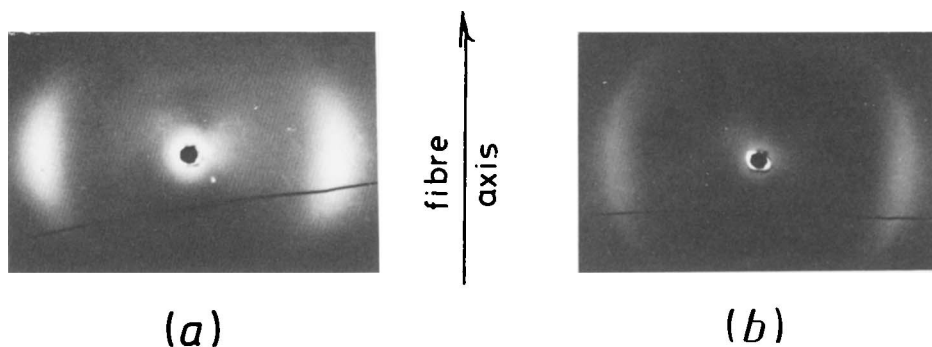
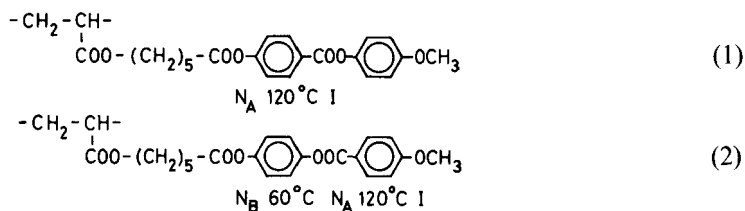
## 2. Experimental

The oriented fibres were prepared by stretching from the liquid-crystal melts and were studied at room temperature. X-ray diffraction patterns were obtained with nickel-filtered  $\text{CuK}_\alpha$  irradiation using a flat plate camera with a specimen-to-film distance of 60.5 mm.

### 2.1. Orientation of nematic polymers

Earlier we showed [7] the possibility of forming two types of nematic structure in polymers having side mesogenic groups. The X-ray diffraction patterns of the first type, having only azimuthal order of the mesogenic groups, are characterized by one diffuse halo at wide angles. The same X-ray diffraction patterns are observed for low molar mass nematics. The second type of nematic order is characterized both by azimuthal and hexagonal order in the plane normal to the nematic director. The corresponding X-ray diffraction patterns have one sharp diffractive maximum at wide angles without any small-angle reflections. We call this nematic mesophase the  $N_B$  phase unlike the usual  $N_A$  phase [7].

The uniaxial orientation of all nematic polymers under study is accompanied by a splitting of the wide-angle maximum into two crescents on the equator. The X-ray diffraction patterns of polymers (1) and (2) forming nematic phases A and B at room temperature are shown in figures 1 (a) and (b).



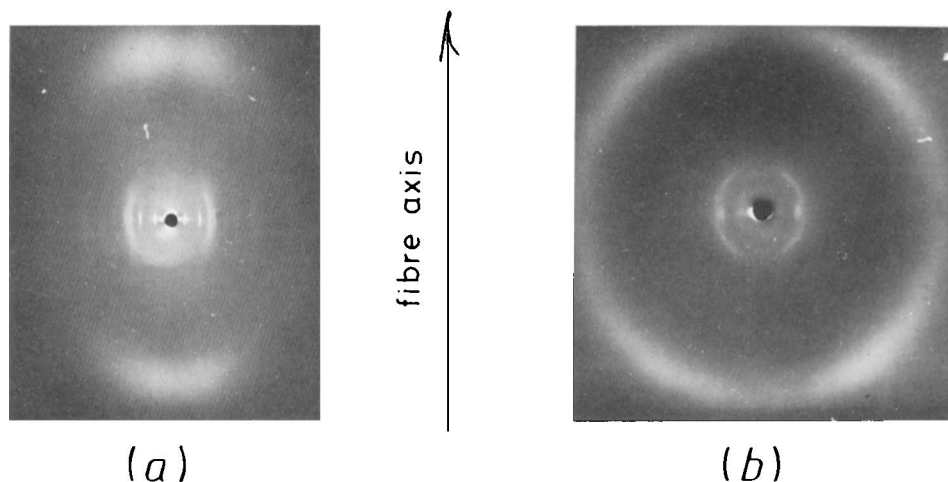
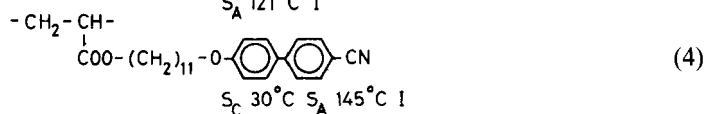
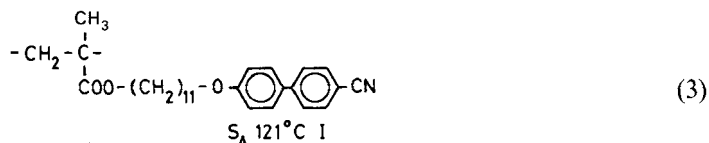


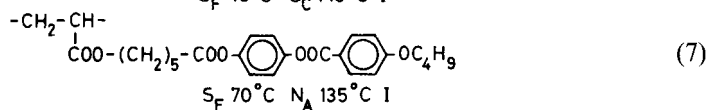
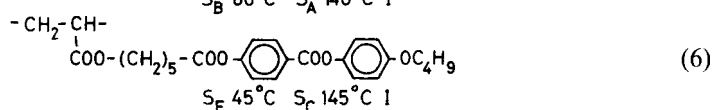
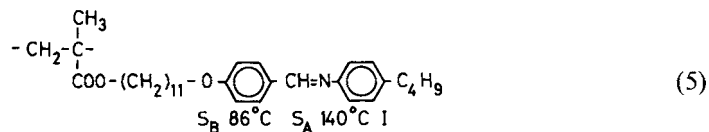
Figure 2. X-ray diffraction patterns of uniaxially oriented polymers (a) (3) and (b) (4) in (a)  $S_A$  and (b)  $S_C$  phases.

### 2.2. Orientation of smectic polymers

Among smectic polymers having side mesogenic groups smectic phases with both two-dimensional order ( $S_A$  and  $S_C$ ) and three-dimensional order ( $S_B$  and  $S_F$ ) have been observed. The polymers in smectic A and C phases are easily oriented by stretching the anisotropic melt. The X-ray diffraction patterns of polymers (3) and (4) oriented in their  $S_A$  and  $S_C$  phases are shown in figures 2 (a) and (b). The polymers existing in



some three-dimensional ordered mesophase cannot be transformed into an oriented state. Their orientation is possible only in two-dimensional ordered smectic phases which are formed at higher temperatures or in the nematic phase. In such cases the transition into the three-dimensional ordered smectic phase proceeds by cooling. Typical X-ray diffraction patterns of oriented samples obtained in this way for polymers (5)–(7) are shown in figure 3.



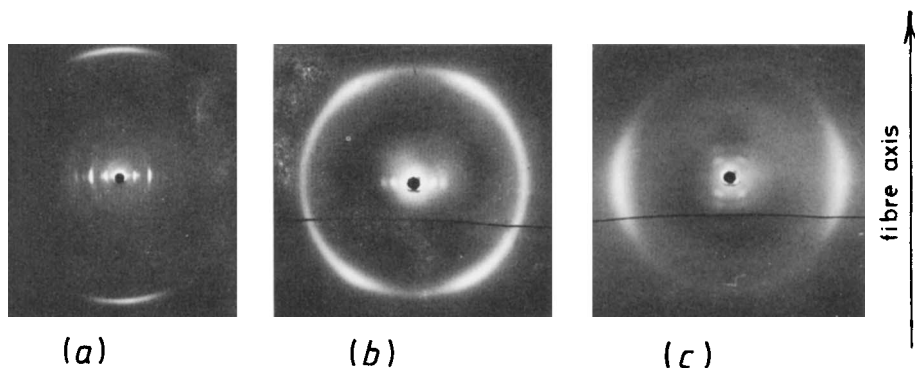


Figure 3. X-ray diffraction patterns of uniaxially oriented polymers (a) (5), (b) (6) and (c) (7) in smectic phases (a)  $S_B$  and (b, c)  $S_F$ . The oriented fibres of polymers (6) and (7) were prepared by stretching from  $S_C$  and  $N_A$  phases, respectively.

We can see from figures 2 and 3 that the X-ray diffraction pattern of samples obtained by orientation in  $S_A$  and  $S_C$  mesophases exhibit small-angle reflections which are always split into two equatorial maxima, while the wide-angle reflections are split either into two crescents on the meridian (for the phases having an orthogonal arrangement of the mesogenic groups,  $S_A$  or  $S_B$ ) or into four crescents (for the tilted arrangement of the mesogenic groups,  $S_C$  or  $S_F$ ). The X-ray diffraction patterns of polymer (7) which forms the smectic phase upon cooling of the sample oriented in the nematic phase consists of two wide-angle crescents and four point-like reflections at small angles. The additional splitting of one of the small-angle reflections into four crescents for polymer (4) is related to the coexistence of two types of layer packing for the mesogenic groups [13, 14].

### 3. Discussion

The wide-angle maximum in the X-ray diffraction patterns of polymers having side mesogenic groups is known [1–7, 9] to be related to the lateral packing of the mesogenic groups. The small-angle reflections correspond to the thickness of the smectic layers.

The orientation of polymers from the nematic mesophase is accompanied by the arrangement of the side mesogenic groups along the fibre axis. Such behaviour of nematic polymers in a mechanical field is a result of features of the deformation of liquid-crystalline polymers characterized by the existence of a region of equally oriented mesogenic groups (domains). The action of various fields (electric, magnetic, mechanical) on low molar mass liquid crystals is known to result in the orientation of the domains. For the polymers under investigation the domains are formed by the mesogenic side groups. Under orientation the long axes of these groups are disposed along the fibre axis. The backbones probably have a random conformation. A schematic diagram of the structure of an oriented nematic polymer is shown in figure 4(a).

The orientation of smectic polymers promotes the slipping of smectic layers and results in their disposition along the direction of the mechanical field. The orientation of the mesogenic groups depends on the type of the smectic mesophase: for  $S_A$  and  $S_B$  phases the mesogenic groups are disposed normal to the smectic layers and to the fibre axis (cf. figure 4(b)), and in the  $S_C$  phase they are tilted (cf. figure 4(c)).

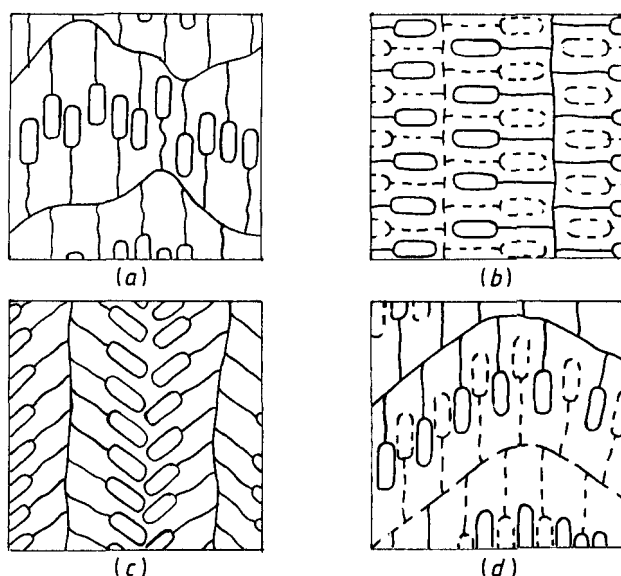


Figure 4. Schemes of macromolecular packing in oriented polymers in (a)  $N_A$  and  $N_B$ , (b)  $S_A$  and  $S_B$ , (c)  $S_C$  and  $S_F$  (oriented in  $S_C$ ) and (d)  $S_F$  (oriented in  $N_A$ ) phases.

The arrangement of smectic layers and mesogenic groups in the  $S_F$  phase depends on the structure of initial melt. Thus, orientation of polymer (6) is possible in the  $S_C$  phase and is accompanied by disposition of smectic layers along the fibre axis, while the angle between the mesogenic groups and the fibre axis is equal to  $34^\circ$ . The transition to the  $S_F$  phase is accompanied by ordering of the mesogenic groups in layers, while their orientation is kept constant. The orientation of polymer (7) proceeds in the nematic phase, and as a result the mesogenic groups are disposed along the fibre axis. The transition into the  $S_F$  phase is accompanied by displacement of mesogenic groups along their long axes keeping the orientation and by the formation of layers tilted to the fibre axis (cf. figure 4(d)).

As the backbones of macromolecules are disposed mainly in the planes of smectic layers their direction should presumably coincide and be disposed along the fibre axis.

In analysis of the splitting of the wide-angle maximum into the equatorial crescents in the X-ray diffraction patterns of oriented nematic comb-like polymers, the authors of [2] have doubted the possibility of the alignment of the mesogenic groups along the fibre axis because of the impossibility of normal disposition of the backbone. An alternative scheme was proposed which included the parallel disposition of backbones and normal disposition of the mesogenic groups. In such a case the macromolecules look like a planar ribbon and the wide-angle diffraction maximum is related to the reflection from these parallel ribbons. This assumption contradicts the well-known experimental data [1–7, 9] on the structure of polymers having side mesogenic groups, according to which the wide-angle reflection corresponds to the distance between the neighbouring mesogenic groups.

Thus the results of this work show the essential dependence of the disposition of the backbones and the mesogenic groups on the type of the polymer mesophase during uniaxial orientation under mechanical stress of comb-like liquid-crystalline polymers.

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