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Liquid crystals from poly(4,4'-methoxybiphenyl methacrylate)

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Résumé.— Les phases liquides cristallines d'un poly(méthacrylate) de 4,4'-biphénylyle ont été étudiées par diffraction des rayons X. Trois phases smectiques ont été décrites à l'aide d'un même modèle de chaîne macromoléculaire sous forme de ruban. Dans la phase smectique S_p , les rubans sont disposés à plat dans des couches avec un espacement égal à l'épaisseur des rubans. Dans la phase smectique S_A , les rubans sont arrangés en simples couches avec un espacement égal à la largeur des rubans. Dans la phase smectique ordonnée S_O , les rubans sont arrangés comme dans la phase S_A mais avec les groupes mésogènes assemblés suivant un réseau bidimensionnel oblique. La texture de type Schlieren observée pour la phase S_p a été analysée en termes de symétrie.

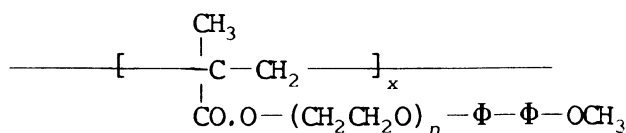
Abstract.— Side-chain liquid crystalline poly(4,4'-biphenyl methacrylate) was studied by X-ray diffraction. Three smectic phases were described using a ribbon-like structural model for the polymer chain. In the smectic S_p phase, ribbons lie flat on their sides to form layers with a spacing equal to the thickness of the ribbons. In the smectic S_A phase, the ribbons stand upright giving layers with a thickness corresponding to the length of one extended monomeric unit. In the ordered smectic S_O phase, the layer thickness also corresponds to one extended repeat unit, and the pendant groups are arranged according to a two-dimensional oblique lattice. The Schlieren texture observed in the S_p phase was analysed in terms of symmetry.

1. Introduction.

Side-chain liquid crystalline polymers have generally been synthesized with a flexible spacer between the pendant mesogenic groups and the polymer backbone [1]. The flexible spacer is currently thought to mechanically decouple the pendant groups from the polymer backbone, allowing for the former to organize in a mesomorphic way and for the latter to adopt a random conformation [2]. A side-chain polymer without flexible spacers has been reported in the literature, which however showed a smectic phase [3]. In this note, another example of such a polymer will be discussed.

The present work is part of a systematic study of side-chain liquid crystalline poly(methacrylates) having 4'-methoxybiphenyl mesogenic pendant

groups and oligo(ethylene oxide) spacers (abbreviated as PM- n in the following) :



The thermal properties [4] and the structure [5,6] of the polymers with $n = 2, 3$ and 4 have been described recently. Their mesomorphic structure was found to be smectic E. The pendant groups are arranged in single layers according to a two-dimensional pseudo-centred rectangular lattice, and the polymer backbones run parallel to the smectic layers along the [110] direction. Using stereochemical and structural arguments, the polymer chains were described to adopt a ribbon-like geometry with the pendant groups hanging

on the same side of the backbone as shown in figure 1.

The liquid crystalline behaviour of the polymers with $n = 0$ and 1 is still under study. As shown in reference [4], thermodynamic and structural equilibrium for these polymers is, indeed, difficult to reach owing, presumably, to their high viscosity. With low-molecular weight PM-O polymers, whose viscosity was not exceedingly high, several interesting structural results have, however, been possible to obtain and will be presented below.

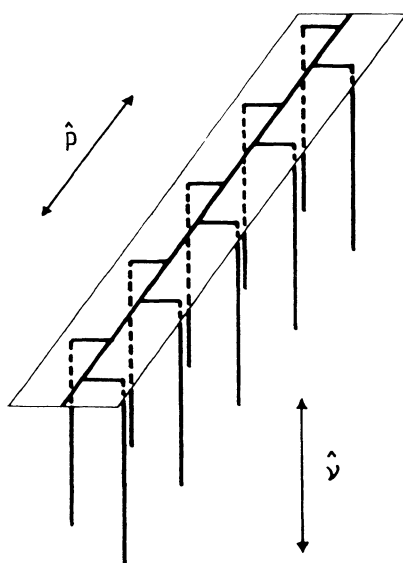
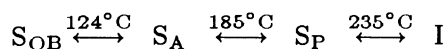


Fig.1.— Schematic view of the ribbon-like geometry of the polymer chain : \hat{v} and \hat{p} represent the directors associated with the pendant groups and the polymer backbones, respectively.

2. Results and discussion.

The PM-O polymer used in the present work (referenced as RP38) was free-radically polymerized [7]. Its weight-average molecular weight was 5.3×10^3 and its index of polydispersity was 1.6 [8]. Its thermal behaviour was studied by thermogravimetry, differential scanning calorimetry, and optical microscopy [4] :



Transition temperatures reported are only approximate due to the equilibrium difficulties stated above.

2.1 The smectic P phase (S_P).— The S_P phase is found to occur at high temperatures, between $185^\circ C$ and $235^\circ C$. Its structure was described previously as “palisades of ribbons stacked in one dimension” [9]. The ribbon-like polymer molecules (Fig.1) lie on their flat sides in layers (Fig.2a) and the polymer backbones are oriented alternately to the right and left. The layer spacing is equal to the thickness of the ribbons (8.4 \AA), and not to the length of the fully extended monomeric unit (about 16 \AA) as is usually the case for smectic phases with the mesogenic groups normal to the layers (Fig.2b).

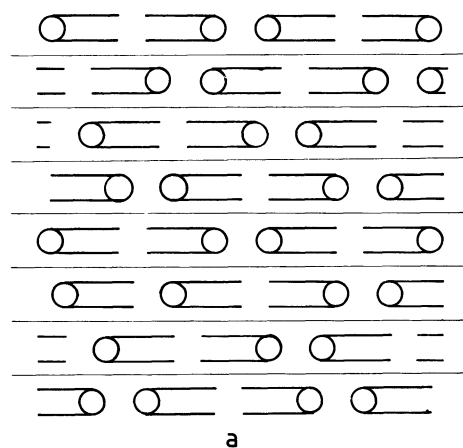


Fig.2.— Schematic view of smectic structures with the ribbons lying flat on their wide (a) or upright (b) with respect to the layers. Open circles and thick straight lines represent the polymer backbones and the double rows of pendant groups along the polymer chains viewed end-on.

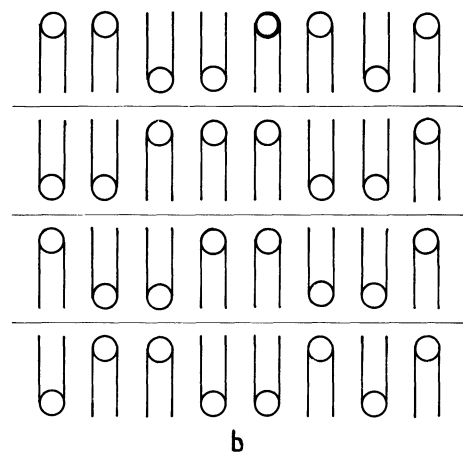


Fig.2b

The texture observed (Fig.3) under the polarizing microscope for this phase is of the classical Schlieren type with two and four-brush point singularities. This is characteristic of a nematic phase, and it is now useful to understand why this texture is observed with a layered structure. It is worth recalling the Schlieren texture is also observed with smectic C phases ; but here only four-brush point singularities can be seen. In smectic C mesophases, the \hat{c} director (which is the direction of the projection of the tilted molecules on the smectic planes) plays a rôle similar to that of the classical nematic \hat{n} director. The absence of two-brush point singularities is due merely to reasons of symmetry : while in nematics rod-like molecules adopt a random up to down orientation, making \hat{n} equivalent to $-\hat{n}$, in smectic C phases the molecules are all pointing in the same direction, resulting in a non-equivalence of \hat{c} and $-\hat{c}$ [10,11]. Because the pendant groups lie parallel to the layers, the smectic P phase described in this paper can be considered as a "special smectic C phase" with a 90-degree tilt angle. The \hat{c} director of this "special smectic C" is, of course, equivalent to the $\hat{\nu}$ director defined in figure 1. As the pendant groups point equally to the right and left (Fig.2a), the \hat{c} director (here $\hat{\nu}$) becomes equivalent to a true nematic director, \hat{n} (\hat{c} becomes equivalent to $-\hat{c}$).



Fig.3.— Optical texture observed for the smectic P phase at 216°C under crossed polars.

With this interpretation, it is clear that the $\hat{\nu}$ directors are macroscopically oriented in the same direction. This means that there is orientational correlation of the mesogenic pendant groups between layers. As can easily be seen from the CPK molecular models, $\hat{\nu}$ and \hat{p} must be strongly cou-

pled, all the more as the PM-O polymer has no flexible spacers. The polymer backbones must hence also be oriented parallel to one another on a three-dimensional macroscopic scale, which implies that the polymer chains are in an extended rather than a random walk conformation.

2.2 The smectic A phase (S_A).— The S_A phase, characterized by typical fan textures under the microscope [4], was found to occur in the temperature range between 124 and 185°C. To confirm the smectic A nature of the material, X-ray patterns of magnetically (1.2 T) oriented samples were registered (Fig.4.). These consist of three sharp, equidistant, and very slightly arced Bragg reflections in the small-angle region, indicative of a lamellar structure with the layers oriented perpendicular to the magnetic field. The layer thickness of 15.8 Å corresponds to the length of one fully extended monomeric unit. The X-ray patterns also exhibit diffuse crescent-shaped scattering in the wide-angle region at about 4.5 Å. This scattering was oriented parallel to the direction of the magnetic field indicating that the pendant groups are consistently parallel to the field and perpendicular to the smectic layers.

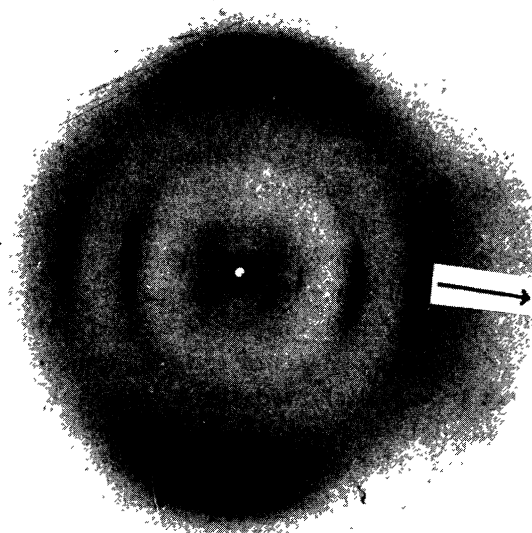


Fig.4.— X-ray pattern of the magnetically oriented smectic A phase (arrow shows the field direction).

Using the same ribbon-like structural element considered for the S_P phase, the smectic layers can be described as formed by the packing of upright ribbons as shown in figure 2b. As with the

high-temperature S_P phase, the ribbons in S_A are expected to be parallel to one another within the layers, presumably with little positional correlation between adjacent ribbons. However, no Schlieren textures can be detected with S_A as \hat{p} is not an optical director. X-ray diagrams taken with fibers drawn from the melt and annealed in the S_A temperature range confirmed the structure just described and showed that the smectic layers are oriented parallel to the draw direction.

It is worth noting in the small-angle region of the X-ray patterns (Fig.4) the presence of four weak and very diffuse spots paired to form two diffuse streaks parallel to the smectic layers. The Bragg spacing of the streaks roughly corresponds to twice the smectic-layer thickness, indicating a tendency towards a modulated S_A structure [12]. In each smectic layer there is a tendency for "ferroelectric" clustering of the ribbons, and between smectic layers, there is a tendency for "antiferroelectric" stacking of the cluster. The wavelength of the in-plane modulation (roughly 30 Å), related to the correlation between clusters, is of the order of three to four ribbon thicknesses.

2.3 The smectic OB phase (S_{OB}).— The S_{OB} phase was found to occur at temperatures below 124°C. Its optical texture was similar to that of S_A [4]. The X-ray patterns registered with magnetically oriented samples shown in figure 5 consisted of three to four sharp, equidistant, and rather slightly arced (although more so than in S_A) Bragg reflections in the small-angle region, indicative of a lamellar structure with the layers oriented perpendicularly to the magnetic field. The layer spacing measured equal to that of S_A , is consistent with a single-layered arrangement of upright ribbons as shown in figure 2b. In the wide-angle region and in a direction perpendicular to that of the magnetic field, the X-ray patterns showed three rather sharp and rather slightly arced Bragg reflections at 4.89, 4.38, and 3.92 Å coming from the lateral ordered packing of the mesogenic pendant groups. Considering the packing of the pendant groups alone, these reflections can be readily indexed as the 010, 100, and 110 reflections from a two-dimensional oblique lattice with the cell parameters $a = 4.61$ Å, $b = 5.15$ Å, and $\gamma \cong 108^\circ$ (Fig.6). The molecular area per pendant group, $S = ab \times \sin \gamma = 22.6$ Å², is in agreement with the usual values obtained with ordered rod-like smectics.

Fig.5.— X-ray pattern of the magnetically oriented smectic OB phase (arrow shows the field direction).

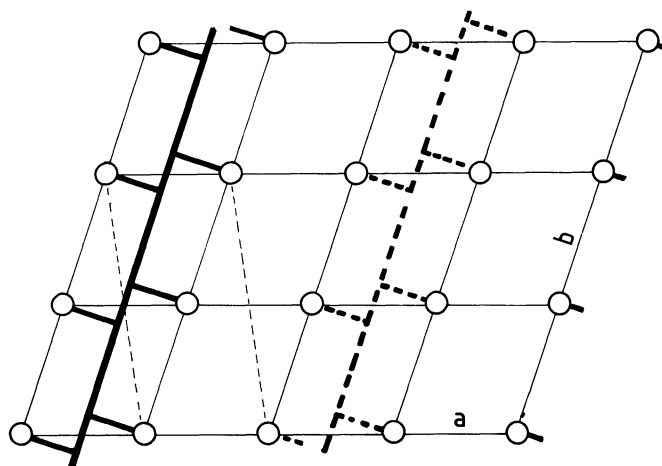


Fig.6.— Two-dimensional oblique lattice describing the packing of the pendant groups. In dashed lines, the unit cell corresponding to the pseudo-centred, deformed rectangular lattice is shown. Circles represent the pendant groups viewed end-on, and thick lines represent polymer backbones.

The first neighbours around each pendant group are in the [100], [010], and [110] directions and located at distances of 4.61, 5.15, 5.76 Å respectively. Knowing from CPK molecular models that the distance between every other pendant group along the polymer chain is about 5 Å, it is clear that the polymer backbones in the layers must run along the [010] direction, as illustrated in figure 6. The lateral distance between adjacent polymer chains is 8.8 Å, in agreement with

the known thickness of the ribbons. It is interesting to note that the packing of the polymer chains in the oblique lattice here is very close to that of the smectic E phase seen for the higher homologs of PM-O where the polymer chains run along the [110] direction of the pseudo-centre rectangular lattice [5,6]. The oblique lattice can indeed be considered as a slightly deformed pseudo-centred rectangular lattice with the cell parameters $A = |a| = 4.61 \text{ \AA}$, $B = |a + 2b| = 9.91 \text{ \AA}$, and $\Gamma = 82^\circ$. The slight difference between the two lattices is obviously due to the difference in the constraints caused by the lack of flexible spacers in PM-O.

3. Experimental.

The custom-made X-ray camera used was equipped with two bent gold-plated glass mirrors

crossed to give a point-“focused” direct beam. It used Ni-filtered copper radiation from an Elliott GX20 rotating anode X-ray generator. With a sample to film distance of 100 mm, it was aligned to allow registration of Bragg reflections in the spacing range from 3 to 100 \AA with a resolution of about 1000 \AA . Samples were oriented magnetically in the X-ray beam using a custom-made magnetic sample holder. This was composed of a 1.2T permanent magnet with X-ray beam passages allowing for the study of the orientation parallel and perpendicular to the magnetic field. The sample holder was electronically thermostated between room temperature and 250°C within 1°C; the variation of the magnetic field was reversible and less than 3 % over this temperature range.

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