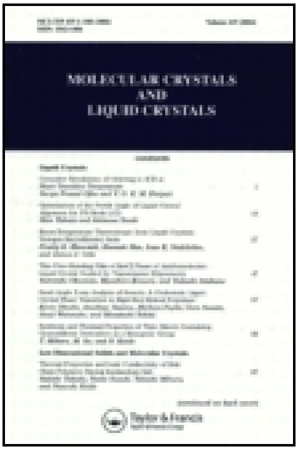

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X-Ray Investigations of +2M4P8BC Ferroelectric Liquid Crystals

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X-RAY INVESTIGATIONS OF +2M4P8BC FERROELECTRIC LIQUID CRYSTAL

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Abstract The X-ray diffraction patterns from aligned smectics G*, J*, I* and C* of ferroelectric liquid crystal +2M4P8BC were obtained by using electric field. New symmetry of molecular packing in plane normal to the molecular long axes for smectic I* is presented.

INTRODUCTION

The symmetry of the electric field is ∞m and it belongs to limiting point-group symmetries. For this reason each crystal which has this symmetry or its subgroup could be a potential ferroelectric crystal. Meyer et al.[1] on the basis of group symmetry considerations found that chiral smectic C phases of symmetry C_2 might exhibit ferroelectric behaviours. The first ferroelectric liquid crystal DOBAMBC was discovered in this way. Recently some ferroelectric liquid crystals were investigated among them the 4 -(2′- methylbutyl) phenyl 4′- n - octylbiphenyl - 4 - carboxylate, previously described as 8SI* and recently as +2M4P8BC.[2,3,4,5]

SAMPLE PREPARATION

The S-(+)-4-(2′-methylbutyl) phenyl ester of 4′-n-octylbiphenyl-4-carboxylic acid was obtained in an equimolar reaction of 4′-n-octylbiphenyl-4-carboxylic acid chloride and S-(+)-2′-methylbutyl phenyl carried out in benzene solution in the presence of pyridine. The rough product was purified by recrystalization from methanol-dietyl ether solution and from n-heksane. The purity of the sample was verified by using thin layers and high pressure chromatography. No impurities were detected.

DIFFERENTIAL SCANNING CALORYMETRY AND MICROSCOPIC OBSERVATION

From the DSC and microscopic measurements the following phase sequences and phase transition temperatures for our sample were established:

$$\mathrm{Cry} \underset{52.0}{\overset{53.0}{\rightleftarrows}} G^{*} \underset{-}{\overset{60.5}{\rightleftarrows}} J^{*} \underset{67.5}{\overset{67.0}{\rightleftarrows}} I^{*} \underset{72.5}{\overset{72.5}{\rightleftarrows}} C^{*} \underset{-}{\overset{82.0}{\rightleftarrows}} A$$

$$A \underset{-}{\overset{138.5}{\rightleftarrows}} \mathrm{Chol} \underset{140.0}{\overset{139.5}{\rightleftarrows}} \mathrm{BP} \underset{141.0}{\overset{140.0}{\rightleftarrows}} \mathrm{Iso}$$

The upper temperatures were obtained from the microscopic textures observations and X-ray measurements, while the lower ones were obtained from DSC measurements. There is a large heat of transition $\mathrm{Cry} \rightarrow G^{*}$ (6.1 cal/g) and $G^{*} \rightarrow \mathrm{Cry}$ (1.7 cal/g) and $I^{*} \rightarrow C^{*}$ (1 cal/g). No peak at the transition $G^{*} \rightarrow J^{*}$ was found and small transition heat at $J^* \rightarrow I^*$ (0.07 cal/g) was detected.

X-RAY INVESTIGATIONS

X-ray diffraction photographs were taken with flat plate and Guinier cameras as well as diffractometer method was used. Photographs were obtained using X-ray Cu, Co and Cr radiation filtered by absorption filters, while diffractometer measurements were carried out on DRON-3 diffractometer with Cu radiation monochromatized by Ge flat monochromator. Scintillation counter and automatic chart pattern or step by step measurements were used to register diffraction radiation. Free standing sample was investigated which means that the liquid crystal was kept in a special electric condenser and that it did not contact with any wall in the direction of X-rays. An electric furnace and automatic temperature controller enabled temperature measurements with an accuracy of $\pm 0.1^\circ$.

The molecular tilt orientation is one of the significant structural parameters. It serves as a distinguishing feature between smectic phases J^* and G^* [3], but also as an order parameter in continuous phase transitions.[6,7] Figure 1 shows the dependence of tilt angle as a function of temperature for the SmC^*- SmA transition. From the relation $\Theta \sim |\Delta T|^\beta$ the critical exponent β was determined as $\beta = 0.43 \pm 0.04$.

To obtain aligned samples, several experiments have been carried out with the help of magnetic field of about 1.6T. No order resulted from that. Contrary to the magnetic field, the electric field is very useful in obtaining well aligned samples. In Figure 2, X-ray photographs of the sample at various temperatures and in electric field of about 1.5kV/mm are presented.

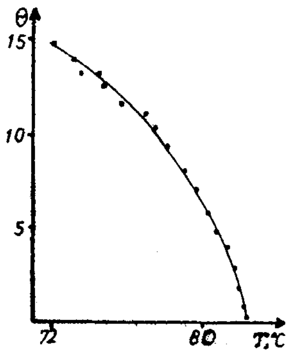

FIGURE 1. Temperature dependence of the tilt angle of the SmC* phase.

RESULTS AND DISCUSSION

From the microscopic textures observations, DSC and X-ray measurements, the following sequences of phases in the +2M4P8BC liquid crystal could be established: Cry $G^* \leftrightarrow J^* \leftrightarrow I^* \leftrightarrow C^* \leftrightarrow A \leftrightarrow$ Chol $\leftrightarrow$ BP $\leftrightarrow$ Iso This phase diagram agrees with the results given by other authors.[2,3] In Figure 2, different symmetry and grain size of the phases G^*, J^*, I^* and C^* is visible. These photographs clearly indicate that there is a long or quasi-long range order in the bond orientation and in tilt orientation in the phases G^*, J^* and I^*, and a liquid like structure within the layers in the smectic

C^*. The X-ray patterns of phases G^*, J^* and I^* can be indexed using the elementary cell parameters given by Budai et al.[3] in the same way as described elsewhere. The photographs of the phases G^*, J^*, and I^* represent fiber pattern and therfore the crystallographic translation along the fiber axis can be calculated directly as for single crystal X-ray rotating photograph. The obtained

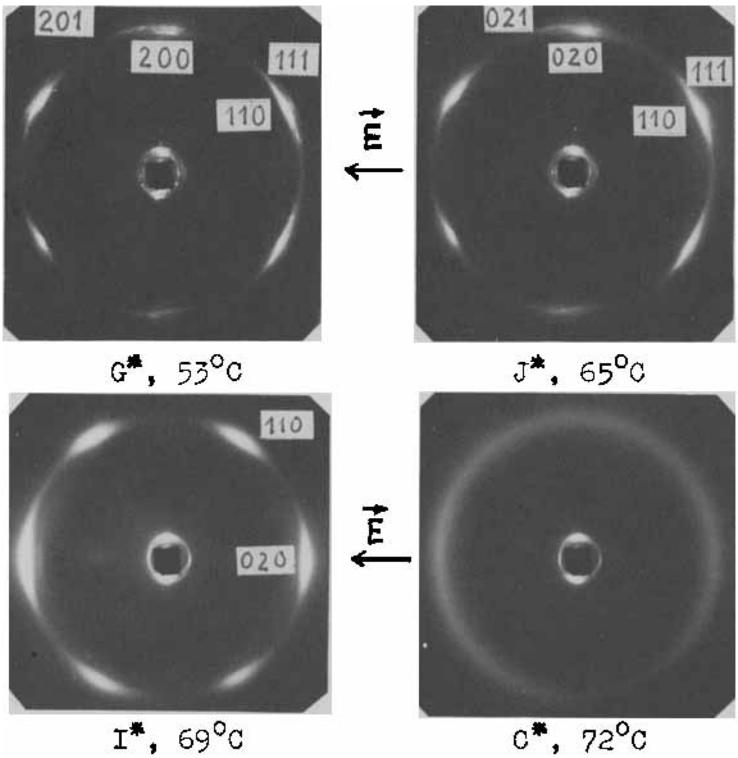

FIGURE 2. X-ray photographs of phases G^*, J^*, I^* and C^* with an electric field of 1.5 kV/mm applied perpendicular to the X-ray beam.

values are $T_{G^*}= T_{J^*}=9.45$ Å and $T_{I^*}=5.48$ Å. These values well agree with lattice constant a of the elementary cells for G* and I* phases and with the b constant for J* phase given by Budai et al.[3] Therefore the fiber axis for G* and I* phases is [100] while for J* phase [010]. However, the texture of G* and J* phases are somewhat confusing because of the presence of 200 and 020 and also 201 and 111 refelexions. It should be noted that there is some scatter of the [100] direction about the fiber axis and for this reason the reflexions usually forbiden for ideal textures do appear on the X-ray photographs.

The spots on the outer ring can be explained as follows. The electric dipole moment which can directly interact with external electric field is perpendicular to the long axis of the molecule For the oom electric field symmetry, the long axes of the molecules are distributed with uniform density in the plane perpendicular to the lines of electric field. We have the following situations: a/ some molecules arranged in smectic layers satisfy the Bragg law and give the inner ring / smectic spots for aligned sample/, b/ some long molecules axes are parallel to the X-ray beam and lead to scattering a symmetry of molecule distribution in the plane perpendicular to the long axes of molecules.[8]

We have measured the correlation length for phases G*,J*,I*,C* and A for a non aligned sample in the same manner as described by Kumar.[9] The corresponding values are: $\xi_{G^*}=920$ Å /at 54°/

ξ_{J^*}=610 Å /at 63°C/, ξ_{I^*} =420 Å /at 68°C/, ξ_{C^*}=60 Å /at 72°C/, ξ_A =30 Å /at 82°C/.

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