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X-RAY STUDY OF SOME LIQUID CRYSTAL HOMO- AND COPOLYMERS

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Abstract The structure of liquid crystal homo- and copolymers based on chiral and achiral monomers was investigated by X-ray diffraction. All investigated polymers have tilted smectic phases with bilayer structures but their X-ray patterns show some features of intensity distribution in reflections related to both the orientation manners and the ratio of the chiral and achiral components. The correlation between the structure of comb-shaped molecules and the chirality of smectic phases is considered using experimental X-ray data, molecular simulation and diffraction calculations from structure models.

INTRODUCTION

Liquid crystal (LC) polymers with chiral centres in side chains are an interesting class of compounds because of perspectives of their practical use as ferroelectric materials. It is known that their LC structure (and therefore their ferroelectric behaviour) may be in accordance with some molecular parameters such as main chain type, mesogenic core, spacer length and molecular weight [1].

The aim of this work was to get information about the structure of comb-shaped copolymers based on chiral and achiral LC monomers. The specify of the chiral component is the position of its chiral centre - in spacer group, but not in the tail group. The investigation of the influence of component formula on the structure of the chiral copolymer is a matter of interest for the search of additional possibility to control its ferroelectric behaviour. Besides the sensitivity of the simulation of one-dimensional section of layer electron density of comb-shaped copolymers for interpretation of their experimental X-ray data was tested in our work..

EXPERIMENTAL

The homo- and copolymers based on the chiral CH_2=CH-COO-CH_2-CH(CH_3)-(CH2)$_2$-COO-C_6H_4-C_6H_4-O-C_8H_{17} and the achiral CH_2=CH-COO-(CH_2)$_6$-O-C_6H_4-COO-C_6H_4-O-C_6H_{13} monomers and prepared by free radical polymerization [2] were investigated by X-ray diffraction. The copolymers with mole content of the chiral component equal to 0.25, 0.50 and 0.75 are labelled further as CPL-25, CPL-50 ,CPL-75, the chiral and achiral homopolymers as CPL-1 and CPL-0 accordingly.

X-ray experiments were performed on aligned in situ samples with Ni-filtered CuK. radiation, registration of scattering intensity on flat films. Angular divergence of X-ray beam at a pinhole collimation was of $1 \cdot 10^{-3}$ radn.. Angular positions (2θ), radial ($\Delta 2\theta$) and azimuth ($\Delta\alpha$) width of reflections of X-ray patterns were measured with a help of microdensitometric system (density scale 0-5)..

Aligned samples were obtained by its cooling at the rate of 1°C/min from the isotropic melt to room temperature, while they were subjected to a magnetic field of 1.2 Tesla. Under these conditions the cooling of the monomers and the copolymers is accompanied by the appearance of an axial texture. These procedures gave negative result for CPL-0. Then the aligning by rotating and extension at viscous flow temperature of this polymer were used.

The X-ray diffraction data were interpreted using the simulation of the layer structure of the homo- and copolymers. The diffraction by model layer structure was calculated in the following way: molecular model - molecular packing model - normal projection of layer electron density - structure factor - scattered intensity. The scattered intensity was calculated as the product of structure factor and one-dimensional interference function [3] and then it was "impaired" by polarization, Lorentz and absorption factors [4].

RESULTS AND DISCUSSION

The chiral homopolymer (CPL-1)

X-ray patterns of CPL-1 aligned in magnetic field are shown in Fig. 1. In temperature range 20-180 °C CPL-1 has two types of X-ray patterns corresponding two liquid crystal phase states. The diffraction and structure parameters of CPL-1 are presented in Table 1.

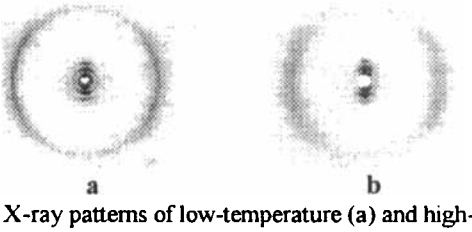

FIGURE 1 X-ray patterns of low-temperature (a) and high-temperature (b) smectic phases of CPL-1 aligned by magnetic field

X-ray pattern of CPL-1 before 120 °C has three multiple narrow crescent maxima in small-angle region and one narrow crescent wide-angle maximum, Fig. 1-a. This pattern is conformed to smectic phase with position correlation of the polymeric side groups within the layers. It may be smectic F* (or I*) phase with tilt angle of the side groups in smectic layers equal to 36° that follows from the correlation of doubled side group length and bilayer spacing (68 · and 52 · accordingly). The smectic B phase with overlap of side groups in bilayers is ignored in our discussion on the basis of the calculation of the diffraction by the model structures carried out earlier [3].

At temperature higher than 120 °C the polymer goes into another smectic state without position ordering of polymeric side groups because wide-angle maximum became more

broad and diffusive, Fig. 1-b. This is an attribute of smectic C* phase. The tilt angle of side groups became larger in this phase (40°).

TABLE 1 Diffraction and structure parameters of CPL-1

Aligning by	Phase, T °C	Reflection	Intensity	d ± Δd ·	Δ(2θ) 10^{-3} radn.	Δ · degr.
Magnetic field	Sm.F* 25	M_1	1	52.7 ± 2.4		54
		M_2	0.64	26.1 ± 1.0	5.69	
		M_3	0.09	17.3 ± 0.4	6.49	
		E		4.51 ± 0.05	19.5	78
Magnetic field	Sm.C* 149	M_1	1	49.7 ± 2.4		56
		M_2	0.87	24.6 ± 1.0	6.62	
		M_3	0.25	16.7 ± 0.4	7.68	
		E		4.51 ± 0.05	83.6	80

The wide azimuth smearing of equatorial reflections (more wide than of meridional reflections) at the absence of their azimuth splitting is the witness of helicoidal structure of both phases (see Δα in Table 1). The magnetic field is not able to untwist this structure.

The achiral homopolymer (CPL-0)

CPL-0 has the following scheme of phase transitions: Glass-32°C-Sm.-120°C-Isotr.liq..

X-ray patterns of CPL-0 aligned by twisting and extension have one pair each of diffuse equatorial reflections but they have a different number of pairs of meridional reflections (3 and 2 accordingly). The diffuse type of equatorial reflections is an evidence of Sm.A or Sm.C phases. Diffraction and structure parameters of CPL-0 are presented in Table 2.

TABLE 2 Diffraction and structure parameters of CPL-0

Phase, T °C	Alignin by	Reflection	Intensity	d ± Δd ·	Δ(2θ) 10^{-3} radn.	Δ · degr.
Sm. 110	twisting	M_1	1	44.9 ± 2.1		70
		M_2	0.3	22.1 ± 0.9	8.92	
		M_3	0.09	14.5 ± 0.4	12.5	
		E		4.58 ± 0.05	90.2	
Sm. 20	extension	M_1	1	59.0 ± 2.4	8.89	54
		M_2	0.29	29.9 ± 1.1	10.5	
		E		4.49 ± 0.05	63.2	

Both samples of CPL-0 have relatively weak alignment but they have appreciable differences in structure determined by alignment method. The sample aligned by twisting has smaller interlayer period and radial width of meridional reflections (that is longer interlayer correlation length) but greater radial width of equatorial reflections (that is shorter intralayer correlation length) than the sample aligned by extension. In the first case experimental interlayer diffraction best of all conforms with a bilayer tilted structure (see Figure 2) as to the number of visible reflections of the interlayer diffraction and the ratio of their intensities (1 :0.30 : 0.09 and 1 : 0.48 : 0.07 accordingly). In the second case the bilayer structure must have smaller tilt angle (than

48°) and apparently the overlap of side groups. Therefore both sample of CPL-0 have smectic C structure but with specific features.

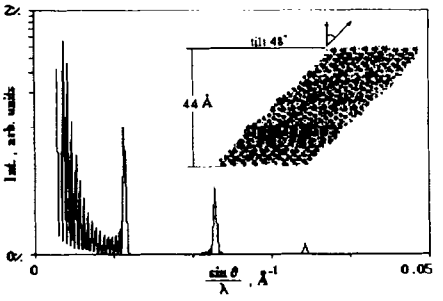

FIGURE 2 The diffraction by the model of bilayer structure of CPL-0 aligned by twisting

CPL-75

The X-ray patterns of CPL-75 aligned in the magnetic field (see Figure 3) have three pairs each of small-angle reflections on their meridians and one pair each of wide-angle

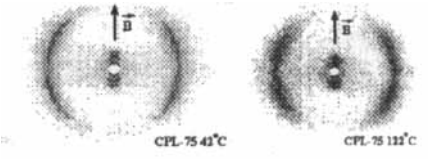

FIGURE 3 X-ray patterns of CPL-75 in low- and high-temperature smectic phases

reflections splited on azimuth (sharp or diffuse in relate of intralayer structure). These patterns are conformed to Sm.F* (or I*) and Sm.C* structures with tilt angle equal to 40°. Their helicoidal structure looks untwisted at least partly (a book-shelf structure). Diffraction and structure parameters of CPL-75 are presented in Table 3 .

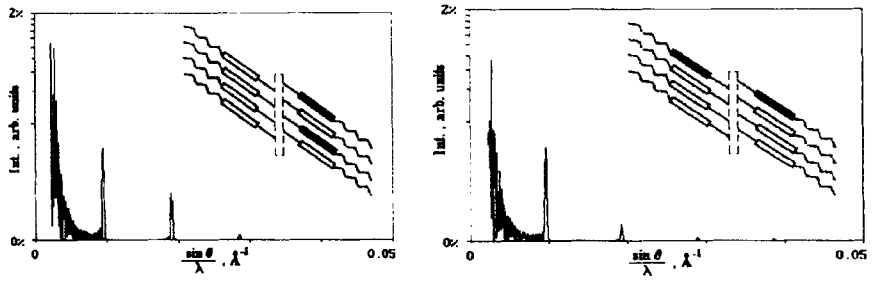

FIGURE 4 The molecular models of CPL-75 (achiral side groups are dark) and diffraction by bilayer structure

The structure model of CPL-75 with asymmetrical bilayers (because of the arrangement of the achiral components mainly in one of two sublayers) has better agreement with experimental data (as to the number of visible reflections of the interlayer diffraction and the ratio of their intensities) than that with symmetrical bilayers, Fig. 4.

The ratios for the first model and for the experimental data are equal to 1 : 0.49 : 0.06 and 1 : 0.44 : 0.08 accordingly.

TABLE 3 Diffraction and structure parameters of the copolymers

Copo-lymer	Aligned by	Phase T, °C	Reflex	Int. arb.units	d ± Δd	Δ(2θ) 10^{-3} radn.	Δα degr.
CPL-75	magn. field	Sm.F* (or I*) 20°	M_1	1	52.2 ± 2.4		43
			M_2	0.44	26.1 ± 1.0	9.81	
			M_3	0.08	17.7 ± 0.6	10.3	
			E		4.49 ± 0.05	38.9	30
CPL-75	magn. field	Sm.C* 122°	M_1		51.0 ± 2.4		54
			M_2		25.2 ± 1.0	11.4	
			M_3		17.2 ± 0.6	11.5	
			E		4.61 ± 0.05	49.0	44
CPL-50	magn. field	Sm.F* (or I*) 20°	M_1	1	52.1 ± 2.4		36
			M_2	0.40	27.8 ± 1.0	9.57	
			M_3	0.10	18.4 ± 0.6	10.3	
			E		4.48 ± 0.05	36.7	70
CPL-50	magn. field	Sm.C* 110°	M_1		53.5 ± 2.4		50
			M_2		26.8 ± 1.0	12.0	
			M_3		17.9 ± 0.6	13.0	
			E		4.64 ± 0.05	71.5	80
CPL-25	magn. field	Sm.F (or Sm.I) 20°	M_1	1	53.3 ± 2.4		24
			M_2	0.56	26.7 ± 1.0	7.80	
			M_3	0.14	17.6 ± 0.6	9.11	
			E		4.43 ± 0.05	40.5	36
CPL-25	magn. field	Sm.C 122°	M_1		54.3 ± 2.4		40
			M_2		27.8 ± 1.0	9.80	
			M_3		18.3 ± 0.6	12.0	
			E		4.58 ± 0.05	83.7	60

CPL-25

The X-ray patterns of CPL-25 aligned by magnetic field are shown in Figure 5. The patterns have small-angle reflections splited on azimuth and wide-angle reflections (sharp or diffuse in relate of phase type) on their equator. These patterns are conformed to the structures with skewed smectic layers (chevron structure) and the polymeric side groups aligned along a magnetic induction vector. Diffraction and structure parameters of CPL-25 are presented in Table 3.

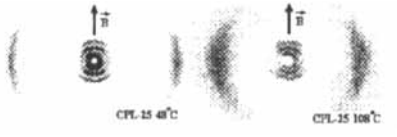

FIGURE 5 X-ray patterns of CPL-25 in low- and high-temperature smectic phases

Both smectic phases of CPL-25 have bilayer structures without a helical twisting (tilted Sm.F or I and Sm.C phases). The tilt angle of side groups to the smectic plane normal is equal to 37° (in Sm.F phase) and 40° (in Sm.C phase). The structure model of

CPL-25 with asymmetrical bilayers has better agreement with experimental data (as to a ratio of the intensities in the reflections of interlayer diffraction) than that with symmetrical bilayers, Figure 6. The ratios for the first model and for the experimental data are equal to 1 : 0.30 : 0.13 and 1 : 0.37 : 0.14 accordingly.

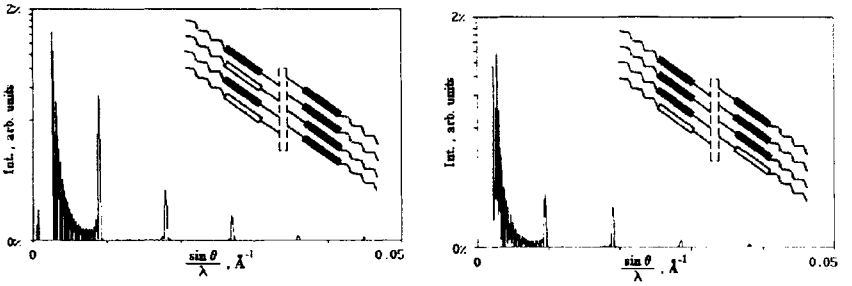

FIGURE 6 The molecular models of CPL-25 and diffraction by bilayer structure (achiral components are dark)

CPL-50

The X-ray patterns of CPL-50 aligned in the magnetic field are shown in Figure 7. These patterns have three pairs each of meridional reflections and one pair each of equatorial reflections (sharp or diffuse). The patterns are conformed to the tilted bilayer smectic phases with the tilt angles equal to 37° (low-temperature Sm.F* or Sm.I* phase) and 39.5° (high-temperature Sm.C* phase). The azimuth smearing of equatorial reflections substantially more wide than of meridional reflections at the absence of their azimuth splitting (as CPL-1 has) is the witness of helicoidal structure of both phases (see $\Delta\alpha$ in Table 3). The magnetic field is not able to untwist this structure.

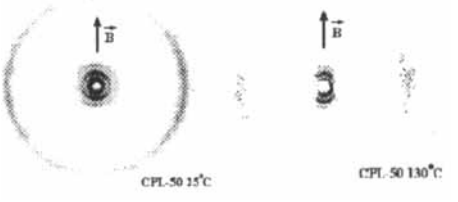

FIGURE 7 X-ray patterns of CPL-50 in low- and high-temperature smectic phases

The calculations of the diffraction by the models of bilayer structures showed that the model with the same proportion of the chiral and achiral components in both sublayers (symmetrical bilayers) have better agreement with experimental data (by the ratio of the intensities in the reflections of interlayer diffraction) than the models with different ratios of the components (asymmetrical bilayers), Figure 8. . The ratios for the first model and for the experimental data are equal to 1 : 0.46 : 0.07 and 1 : 0.49 : 0.12 accordingly. This model does not exclude the fact that CPL-50 may be a block-copolymer with the short chiral and achiral sindiotactic molecular fragments.

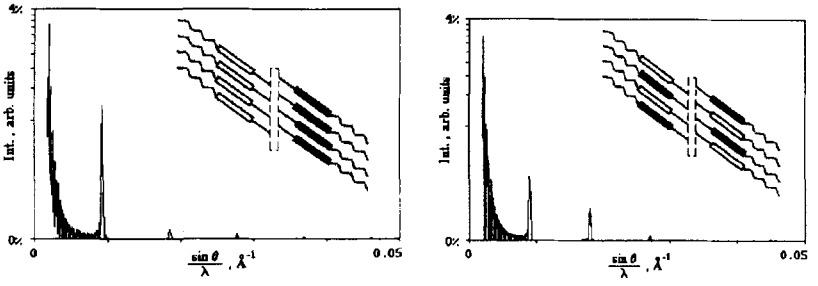

FIGURE 8 The molecular models of CPL-50 and diffractions by bilayer structure

CONCLUSION

Our research showed that all investigated copolymers have two tilted smectic phases each. and their chirality can be controled changing the ratio of the chiral and achiral components. The presence of the achiral component in CPL-75 made possible to untwist helicoidal structure by magnetic field that is apparently connected with its distribution mainly in one of two sublayers (asymmetrical bilayers). It is not a success to untwist a helicoidal structure by the same magnetic field in chiral phases with symmetrical bilayers (CPL-1 and CPL-50). These results look unexpected as only CPL-50 exhibit ferroelectric behaviour [5]. Latter on we shall investigate the temperature behaviour of these copolymer structures aligned not only by magnetic field but by electric field too.

The electron density projection on a bilayer normal is sufficiently sensitive to both a component content in sublayers and a side group tilt therefore the method based on its simulation and a calculation of interlayer diffraction deserves further development effort.

Acknowledgements

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