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THERMAL ANALYSIS AND X-RAY STUDIES OF CHIRAL FERROELECTRIC LIQUID CRYSTALLINE MATERIALS AND THEIR BINARY MIXTURES

Dusanka Ž. Obadović[1], *Anikó Vajda*[2], *Maya Garić*[1], *A. Bubnov*[3], *Vera Hamplová*[3], *M. Kašpar*[3] *and Katalin Fodor-Csorba*[2*]

[1]Department of Physics, Faculty of Sciences, University of Novi Sad, Trg D. Obradovi ća 4, Novi Sad, Serbia and Montenegro
[2]Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 49, Hungary
[3]Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Prague, Czech Republic

Thermal properties of a homologous series of ferroelectric liquid crystals *S*-(–)-[4-(2-*n*-alkoxy-propionyloxy)]biphenyl-4'-[*n*-alkoxy-(3,5-dimethyl)]benzoate have been investigated by polarizing optical microscopy and differential scanning calorimetry. The mesophases were identified and confirmed by X-ray too. Three binary mixtures were prepared from the individual homologues. In one of the mixtures (Mix1), the ferroelectric SmC* phase has broadened and became enantiotropic. This mesophase remained monotropic in the other two mixtures (Mix2, Mix3). The chiral nematic N* phase did not appear in Mix1, but remained monotropic for the other two mixtures. Two molecular parameters, the layer spacing and the average intermolecular distance have been calculated from the X-ray results for the homologues and their mixtures. An intercalated tail-to-tail packing of molecules was found both in the single compounds and their mixtures resulting in the layer spacing about half of the molecular length of the single compounds.

Keywords: *DSC, ferroelectric liquid crystal, intermolecular distance, layer spacing, phase transition, X-ray diffraction*

Introduction

The ferroelectric behaviour of the lactic acid derivatives has been investigated intensively within last several years. Homologous series of the *S*-(–)-4-(2-*n*-alkoxy-propionyloxy)biphenyl-4'-[*n*-alkoxy]benzoates (denoted as H *n*/*m* series) [1], *S*-(–)-4-(2-*n*-alkoxy-propionyl oxy)biphenyl-4'-[*n*-alkoxy-(3-methoxy)] benzoates (denoted as MO *n*/*m* series) [2], *S*-(–)-4-(2-*n*-alkoxy-propionyloxy)biphenyl- 4'-[*n*-alkoxy-(3-methyl]benzoates (denoted as M *n*/*m* series) [3] and *S*-(–)-4-(2-*n*-alkoxy- propionyloxy)biphenyl-4'-[*n*-alkoxy(3,5-dimethyl]benzoates (denoted as DM *n*/*m* series) [4] were investigated in point of view of mesomorphic and electro-optical properties.

Identification of the mesophases of new compounds can be carried out by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC), but in some cases the mesophases should be further investigated by X-ray measurements too. There are many examples in the literature where the characterization of the mesophases was supported by X-ray data, here only few of them are cited [5, 6].

Here we present the investigation carried out on the DM *n*/*m* series. The synthesis of these ferroelectric liquid crystals *S*-(–)-4-(2-n-alkoxy-propionyloxy) biphenyl-4'-[*n*-alkoxy-(3,5-dimethyl)]benzoate (denoted as DM *n*/*m*) derived from the O-substituted *S*-(–)-lactic acid was described earlier [4]. General formula of the studied materials is depicted in Fig. 1.

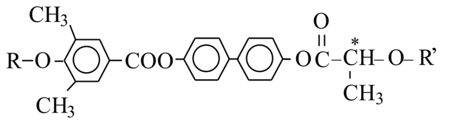

Fig. 1 Chemical structure of DM n/m; where R=C_nH_{2n+1} and R'=C_mH_{2m+1}

The peculiarities of the molecular arrangements in mesophases of ferroelectric mixtures have been studied intensively by various authors [7, 8]. Many efforts have been done in order to establish the rules of molecular interactions in different type of ferroelectric liquid crystalline mixtures.

The aim of this work was to characterize the mesomorphic properties of the six representatives of homologous series of *S*-(–)-4-(2-*n*-alkoxy- propionyloxy)biphenyl-4'-[*n*-alkoxy-(3,5-dimethy)]benzoates and three of their mixtures. These investigations were carried out with POM, DSC and X-ray studies on the homologous series and their binary mixtures.

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* Author for correspondence: fodor@szfki.hu

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Experimental

Optical study was performed using polarization optical microscope Amplival Pol-U with a Boetius hot-stage. The heating rate was 4°C min^{-1}, the cooling rate was not controlled. Phase transition temperatures was checked by DSC (Pyris Diamond Perkin-Elmer 7) using cooling and heating runs at a rate of 5 K min^{-1}. The samples of 3–8 mg were placed in a nitrogen atmosphere and hermetically sealed in aluminium pans. Non-oriented samples were investigated by the X-ray diffraction in transmission geometry using a conventional powder diffractometer, Seifert V-14, CuK_α radiation at 0.154 nm, with an automatic high temperature kit Paar HTK-10. The layer spacing (*d*), and the average intermolecular distance between the long axes of neighbouring parallel molecules (*D*) were performed using the Bragg law: $n\lambda=2d\sin\theta$. The parameters *d* and *D* were calculated from the position of the small angle and large angle diffraction peak, respectively [9, 10]. In the case of the N* phase, the *d* value corresponds to the mean repeat distance along the director or the length of the molecule in fact.

Results and discussion

The ferroelectric lactic acid derivatives and their mixtures were investigated by POM and DSC methods. The phase transition temperatures obtained by POM and DSC with almost the same heating and cooling rate are in a good accordance. The X-ray measurements were carried out at a definite temperature in the mesophase formed; no X-ray investigations were done at the phase transition temperatures. Characteristic textures of the Blue (BP), N*, SmC* phases and their transitions are depicted in Fig. 2.

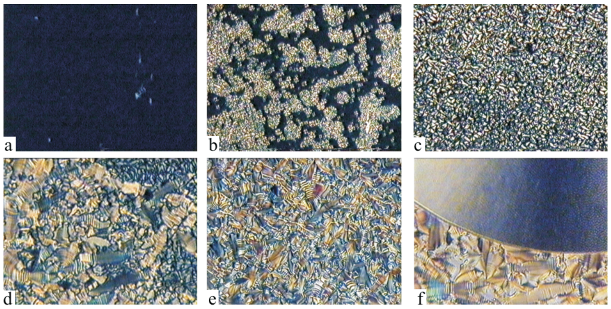

Fig. 2 Characteristic textures of the mesophases observed on cooling of DM 7/10 compound: a – BP phase at 54.0°C, magnification=80; b – transition between BP and N* phases at 49.8°C, magnification=80; c – N* phase at 48.0°C, magnification=160; d – transition between N* and SmC* phases at 45.4°C, magnification=160; e – SmC* phase at 44.0°C, magnification=80; f – crystallization at 43.0°C, magnification=160

Table 1 Composition of mixtures

Code	Mixture composition/mass%
Mix1	50% – DM 7/6+50% – DM 7/10
Mix2	60% – DM 10/8+40% – DM 10/12
Mix3	60% – DM 7/5+40% – DM 12/12

The composition of mixtures is summarized in Table 1. Phase transition temperatures of the single compounds and their binary mixtures are presented in Table 2. Melting points, (*m.p.*), sequence of phases, phase transition temperatures, phase transition enthalpies and molecular masses, were measured and calculated, respectively.

The mixtures Mix1 and Mix2 are composed from the members of the DM *n*/*m* series with chiral chains differing from each other by four carbon atoms, namely from DM 7/6 and DM 7/10; DM 10/8 and DM 10/12, respectively.

It was established for mixtures Mix1 and Mix2 that the temperature range of the chiral smectic phase (SmC*) has been broadened. Moreover, the SmC* phase became enantiotropic for the Mix1. This phase remains monotropic in mixture Mix3 where the difference of the terminal chains is larger than four carbon

Table 2 Phase sequence and phase behaviour of the DM *n*/*m* homologues and their mixtures

Code, *n*	*m.p.*/ °C	mol. mass/ g mol^{-1}	Phase transition/°C; enthalpies, [ΔH/kJ mol^{-1}]								
			Cr		SmC*		N*		BP		Iso
DM 7/5	68.3 [48.00]	574	•	30.0 [msc]	•	32.6 [–1.66]	•	54.1 [–0.52]	–		•
DM 7/6	59.9 [44.30]	588	•	30.0 [msc]	•	35.8 [–1.71]	•	52.6 [–0.47]	–		•
DM 7/10	73.0 [64.50]	644	•	43.0 [x]	•	45.4 [x]	•	49.8 [–0.77]	•	56.0 [msc]	•
DM 10/8	62.3 [65.30]	658	•	38.0 [msc]	•	49.1 [–2.30]	•	53.1 [–1.05]	–		•
DM 10/12	74.0 [67.30]	714	•	51.5 [–57.80]	•	55.7 [x]	–		–		•
DM 12/12	73.9 [73.40]	742	•	42.8 [–35.10]	•	57.0 [–18.30]	–		–		•
Mix1	41.6 [10.20]	616	•	36.1 [–1.54]	•	49.8 [–0.68]	–		–		•
Mix2	56.9 [51.10]	680	•	29.3 [–27.90]	•	47.5 [–1.70]	•	51.4 [–1.29]	–		•
Mix3	51.6 [36.10]	641	•	8.2 [–7.05]	•	32.7 [–0.90]	•	50.2 [–0.90]	–		•

• – the phase exists; – – the phase does not exist; [msc] – determined by microscope only; [x] – not possible to determine the exact value of enthalpy due to phase coexistence; Cr – some type of high ordered crystal phase

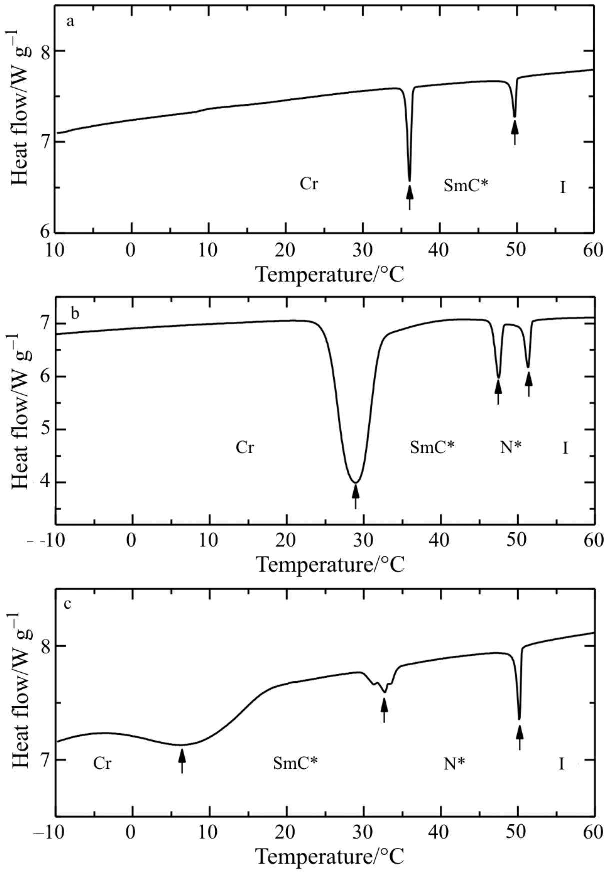

Fig. 3 DSC plots for the studied mixtures on cooling runs:
a – Mix1, b – Mix2 and c – Mix3

atoms (DM 7/5 and DM 12/12). The chiral nematic (N*) phase did not appear in Mix1. The DSC curves of the above mentioned mixtures are depicted in Fig. 3.

X-ray diffraction studies were carried out on the individual compounds and their binary mixtures in all exhibited mesophases. Figures 4 and 5 show the examples of X-ray profiles obtained on the non-oriented samples as a function of the temperature in single compound and mixture, respectively.

In the case of DM 7/10 (Fig. 4), the SmC*, N* and the BP have been identified. The analysis of X-ray diagrams of the SmC* phase transition shows the presence of reflections at small angles (2θ~4.65°), indicating the layer structure, besides the diffuse outer scattering (2θ~22.5°) corresponds to average intermolecular distance between long axes of the neighbouring parallel molecules. The calculation of effective layer thickness *d* and the intermolecular distance *D* gives the value of 22.1 and 4.58 Å, respectively.

The shift of the maximum of the broad peak towards higher angle values indicates higher packing density in the SmC* phase, than in the isotropic (I) and chiral nematic phases, giving the values decreasing with temperature. It was observed for individual

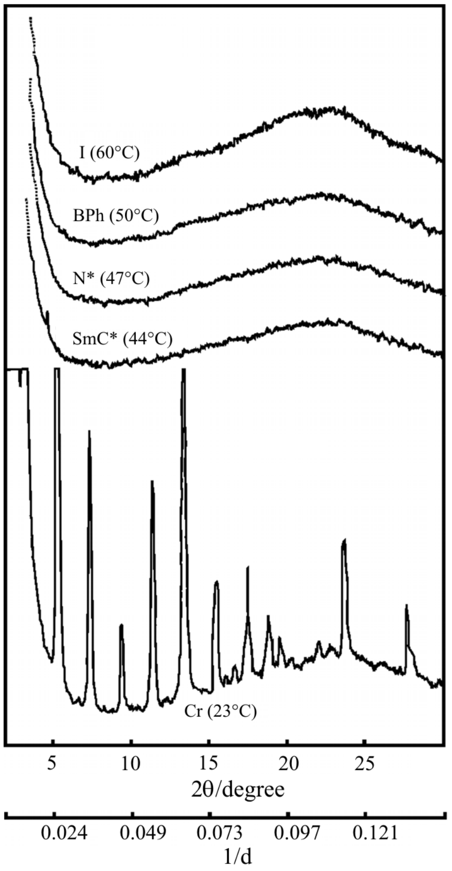

Fig. 4 X-ray diffraction profile for DM 7/10

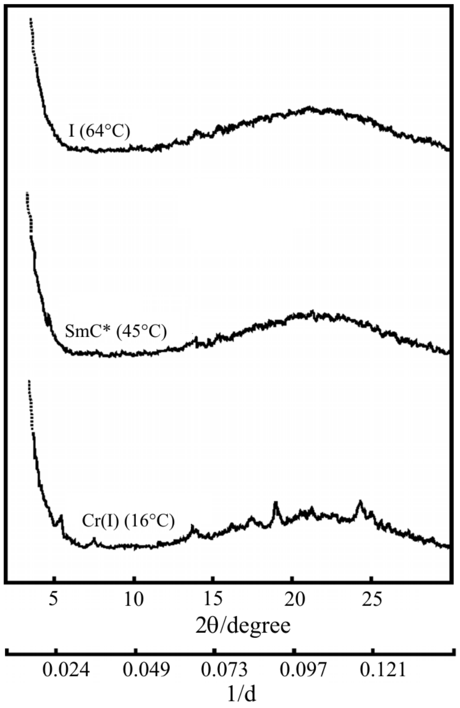

Fig. 5 X-ray diffraction profile for Mix1

Table 3 Molecular parameters of pure compounds and binary mixtures for all observed phases at selected temperature T in °C: angles corresponding to the reflection peaks 2θ in degree, effective layer thickness d in Å (error of measurements δ_d was about ±0.3 Å), average repeat distance D in Å (error of measurements δ_D was about ±0.002 Å). In the N* phase (Mix2) d value corresponds to the mean repeat distance along the director axis

	phase	T/°C	2θ/degree	d/Å	D/Å
DM 7/6	I	61.0	21.35	–	4.832
	N*	45.0	21.60	–	4.776
	SmC*	32.0	5.60	18.3	–
			22.10	–	4.670
DM 7/10	I	60.0	22.00	–	4.670
	BP	50.0	22.00	–	4.670
	N*	47.0	22.30	–	4.628
	SmC*	44.0	4.65	22.1	–
			22.50	–	4.588
Mix1	I	64.0	20.80	–	4.958
	SmC*	45.0	4.85	21.2	–
			21.40	–	4.820
DM 10/8	I	60.0	21.85	–	4.722
	N*	51.0	21.10	–	4.888
	SmC*	41.0	4.85	21.2	–
			22.20	–	4.649
DM 10/12	I	60.0	21.10	–	4.888
	SmC*	52.0	4.45	23.1	–
			5.30	19.4	–
			21.60	–	4.776
Mix2	I	55.0	21.50	–	4.832
	N*	49.0	4.75	21.6	–
			21.35	–	4.798
	SmC*	42.0	4.90	20.9	–
			5.20	19.7	–
			21.50	–	4.790
DM 7/5	I	70.0	21.10	–	4.888
	N*	50.0	21.60	–	4.776
	SmC*	31.0	4.80	21.4	–
			5.20	19.7	–
			22.10	–	4.670
DM 12/12	I	75.0	20.90	–	4.935
	SmC*	54.0	4.60	22.3	–
			5.05	20.3	–
			21.70	–	4.755
Mix3	I	58.0	19.90	–	5.180
	N*	48.0	20.00	–	5.154
	SmC*	31.0	3.70	27.7	–
			19.90	–	5.180

components and their mixtures too. While decreasing the temperature, the position of the small angle reflection is somewhat shifted to the higher angle, indicating an increase in layer spacing of the SmC* phase for all studied compounds (Fig. 4 and Table 3).

If the chain length of the chiral part was changed keeping constant both the core and the non-chiral chain length, (DM 7/6, DM 7/10 and DM 10/8, DM 10/12) intermolecular distance between the long axes of neighbouring parallel molecules in mixtures Mix1 and Mix2 was slightly increased in the SmC* phase, with respect to the single compounds. For Mix2, the calculation of effective layer thickness d, gives the value smaller than that of the component.

If the mixture is composed from molecules with significantly different terminal chains (DM 7/5 and DM 12/12 in Mix3), the packing density of the molecules decreases with respect to the individual components (Table 3). In the case of these mixture, some significant change in d value in SmC* phase respecting to the pure components was observed.

The total length of DM 10/12 molecule was calculated by semi-empirical CAChe/MOPAC/PM5 method (Fig. 6). This approximation gave 45 Å in length of all trans conformation. This value shows evidently an inter-

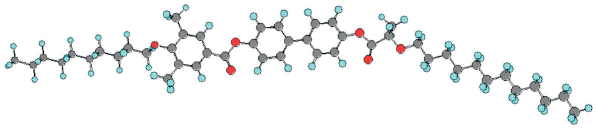

Fig. 6 Optimized structure of DM 10/12, total length of molecule is about 45 Å

calated structure appearing in all mixtures studied. The close intercalated tail-to-tail packing with different intermolecular distances can make understandable that the SmC* phase is enantiotropic or monotropic in the mixtures. The higher dense packing of the molecules in Mix1 most probably helped the formation of the enantiotropic SmC* phase, while the less dense packing of the molecules in Mix3 retains monotropic character of the SmC* phase [11].

Conclusions

The mesomorphic behaviour of ferroelectric lactic acid derivatives as members of DM *n*/*m* series having two methyl groups as lateral substituents was investigated. The individual members show monotropic SmC* phase, probably due to the presence of two methyl groups into 3,5-positions that gives rise to a dramatic change of mesogenic behaviour while comparing to non-substituted compounds or mono-substituted ones [1, 4]. The layer spacing increases with increasing of the chiral chain length.

The ferroelectric phase (SmC*) of the binary mixtures composed from DM *n*/*m* series have shown a shift of this mesophase to the lower temperature range. On the base of the X-ray diffraction data on the crystalline powder of non-oriented samples the molecular parameters, the intermolecular distance, *D*, and interlayer spacing, *d* were determined. In SmC* phase of mixtures Mix1 and Mix2, the parameter *D* increases with respect to the individual components. The effective layer thickness in the Mix1 and Mix2 is smaller than in the pure components that indicate an intercalated tail-to-tail packing of the molecules. This fact most probable is responsible for stabilization of the ferroelectric phase, making it enantiotropic and causes the disappearance of the BP and N* phase. For the mixture Mix3, the packing density of the molecules increased and the *d* value showed a jump.

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