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Broad liquid crystalline temperature range of ferroelectric liquid crystals

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Broad liquid crystalline temperature range of ferroelectric liquid crystals

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Novel ferroelectric liquid crystalline compounds, containing the (*S*)-2-methyl-1-butyl (4-hydroxybiphenyl-4′-carbonyloxy)biphenyl-4-carboxylate mesogenic group and an oligooxyethylene spacer, were synthesized. The mesomorphic properties of these materials were investigated by differential scanning calorimetry (DSC), optical polarizing microscopy (POM) and powder X-ray diffraction measurement. The results indicate that all members of this series exhibit a very broad temperature mesophase range (reaching a maximum around 210°C) including a blue phase (BP), cholesteric (Ch), twist grain boundary A (TGB$_A$), chiral smectic C (S$_C^*$), and smectic X (S$_X$) phases. The mesomorphic properties are discussed and a comparison is made with three phenyl rings of ester core analogues.

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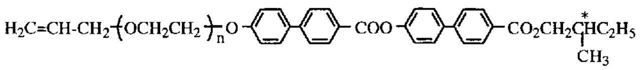
1. Introduction

Ferroelectric liquid crystals (FLCs) [1–3] and ferroelectric liquid crystalline polymers (FLCPs) are under intense development for display applications. An FLC material used for displays should show a smectic phase over a wide temperature range, including room temperature [4]. Moreover, it may be desirable for material to possess large spontaneous polarization, so the FLC devices can be operated at a reduced driving voltage. These properties are influenced by the molecular structures of the liquid crystal compounds. Consequently, it is of interest to synthesize ferroelectric liquid crystal compounds and compositions which exhibit favourable spontaneous polarization values and have smectic character over a wide temperature range, especially at room temperature.

Several side chain liquid crystalline polymers (LCPs) exhibiting a chiral smectic C mesophase have been reported. Ferroelectric properties, for example, spontaneous polarization, have also been reported in these polymers [5–8]. Our research program involving the development of high efficiency FLC materials has entailed designing and synthesizing some novel low mass FLCs and ferroelectric side chain liquid crystalline polymers [9–12]. They exhibit a broad temperature range of chiral smectic C phases and satisfactory electro-optical properties [13].

In this study, a newly designed series of FLCs is synthesized and preliminary characterized. The properties of a biphenyl biphenyl carboxylate mesogenic group with (*S*)-2-methyl-1-butyl chiral tail series are examined, with particular reference made to the effect that the flexible oxyethylene units influence the stabilization of the chiral smectic C phase.

The new series has the general formulae:



MD*n*22A ($n = 0, 1, 2, 3$)

2. Synthesis

The MD*n*22A series compounds ($n = 0, 1, 2, 3$) were synthesized by standard methods. The first step was the esterification of 4-hydroxybiphenyl-4′-carboxylic acid with (*S*)-2-methyl-1-butanol in the presence of diethyl azodicarboxylate and triphenyl phosphine by the method of Mitsunobu [14], forming the (*S*)-2-methyl-1-butyl 4-hydroxybiphenyl-4′-carboxylate. The ester produced was purified by column chromatography and then esterified with 4′-allyloxybiphenyl-4-carboxylic acid, 4′-(2-allyloxyethoxy)biphenyl-4-carboxylic acid, 4′-(2-(2-allyloxyethoxy)ethoxy)biphenyl-4-carboxylic acid, or 4′-(2-(2-(2-allyloxyethoxy)ethoxy)ethoxy)-4-biphenylcarboxylic acid. As a result, the final liquid crystal materials could be produced.

The final products were carefully purified by flash chromatography with silica gel (200–400 mesh) using *n*-hexane/dichloromethane as the eluant. The collected fractions revealed a single component by thin-layer chromatography. The product purity was verified using

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high performance liquid chromatography. The final product structures were determined by IR, and ^{1}H NMR analysis. Results obtained for each compound agreed with the predicted structures of the target materials.

The new mesogens were characterized by differential scanning calorimetry, optical polarizing microscopy, and high resolution powder X-ray diffraction measurements. The transition temperatures ($\pm 0{\cdot}1$°C) and initial phase assignments for target liquid crystals were determined via thermal optical microscopy using a Nikon Microphot-FX optical polarizing light microscope equipped with a Mettler FP80 thermal control unit. Temperatures and heat capacities of transition were determined by differential scanning calorimetry using a Seiko SSC 5200H in conjunction with a thermal analysis data station (TDS). The material was studied at various heating and cooling rates (5 and 10°C min^{-1}) in an aluminium pan. X-ray diffraction measurements were taken with a Rigaku R-Axis IIC powder diffractometer. Two imaging plate (IP) detectors were used so that reflection spot exposure and readout operations could be performed. This feature provides an increased data accumulation efficiency and minimizes the time required for IP residual image erasure. The monochromatized X-ray beam from nickel-filtered CuK$_\alpha$ radiation with a wavelength of 0·15406 nm was used. A temperature controller was added to the X-ray apparatus for thermal measurements. The precision of the controller was $\pm$ 0·5°C in the temperature range studied.

3. Results and discussion

The phase sequences and the corresponding transition temperatures for the new synthesized series are summarized in table 1. All members of this series exhibit a rich enantiotropic liquid crystalline phase sequence: I–BP–Ch–TGB$_A$–S$_A$–S$_C^*$; except for the shorter chain units ($n = 0, 1$) in which the S$_C^*$ phase is not observed. Note that upper transition temperature for MD022A ($n = 0$) is slightly unreliable as decomposition begins at around 300°C. Representative DSC thermogram and thermal transitions for compound MD322A ($n = 3$) are shown in figure 1. On heating, four endothermic transitions at 58·9, 66, 229·3, and 234·3°C, respectively, are observed. On cooling, all the transitions are reversed with about 15 degrees of supercooling. Obtaining individual transition enthalpies from the BP/Ch and TGB$_A$/S$_A$ phases is relatively difficult due to overlapping. In addition, the transition enthalpy of S$_A$/S$_C^*$ is too small for DSC investigation.

The optical polarizing microscopy study for series MD*n*22A is similar to the results from the previously synthesized series MD*n*12A ($n = 1, 2, 3$) [12]. Unambiguous identification of the nature of the BP, Ch, TGB$_A$, S$_A$, S$_C^*$ mesophases was not deemed possible by optical microscopy observations. In contrast, X-ray diffraction analysis clarifies the smectic mesomorphism of materials. Figure 2 illustrates the powder X-ray diffraction measurements of MD322A at 226, 180, 130, 120, 102, and 62°C, respectively. A broad reflection at wide angles (associated with the lateral packings) and a sharp reflection at small angles (associated with the smectic layers) are shown by all curves, respectively. Curve A exhibits a rather diffuse reflection appearing at around 5·78 Å. This reflection corresponds to lateral spacing of two mesogenic groups; in addition, a very weak reflection at 35·3225 Å which

Table 1. Thermal transition temperatures for the series MD*n*22A.

Compound	n^a	Phase transition/°C (corresponding enthalpy changes mJ mg^{-1})^b Heating/Cooling
MD022A	0	Cr 169·4(58·65) S$_A$ 270(−) TGB$_A$ 272·8(2·58)^c Ch-decomposed ^{d}I 270 Ch 175 TGB$_A$ 172 S$_A$ 91·8(30·16) Cr
MD122A	1	Cr 126(43·4) S$_A$ 272(−) TGB$_A$ 273(3·0)^c Ch 300·7(1·3) I I 295·5 BP 295·4(1·4) Ch 266·7(−) TGB$_A$ 265(3·3)^c S$_A$ 118(5·1) S$_x$ 84·5(19·6) Cr
MD222A	2	Cr 119·6(43·7) S$_C^*$ 172(−)^e S$_A$ 254·5(−) TGB$_A$ 255·3(−) Ch 266(2·2)^c BP 266·5(0·9) I I 266·5 BP 266(1·0)^f Ch 253·5(−) TGB$_A$ 250·2 (2·2)^c S$_A$ 164(−)^e S$_C^*$ 72·9(34·6) Cr
MD322A	3	Cr 58·9(−) S$_x$ 66(15·2) S$_C^*$ 140·5(−)^c S$_A$ 229·4(−) TGB$_A$ 231(−) Ch 234·3(4·3) BP 234·8 I I 231·8 BP 223·6(−) Ch 220(−) TGB$_A$ 216·5(4·2)^c S$_A$ 139(−)^e S$_C^*$ 63·8(1·9) S$_x$ 44·5(10) Cr

[a] *n* according to the scheme.

[b] Cr = crystalline phase, S$_A$ = smectic A, S$_C^*$ = chiral smectic C, TGB$_A$ = twist grain boundary A, Ch = cholesteric phase, BP = blue phase, S$_X$ = unidentified smectic phase.

[c] Δ*H*(Ch–TGB$_A$–S$_A$).

[d] The transition temperatures are influenced by decomposition of the materials.

[e] Enthalpies were too small to be evaluated.

[f] Δ*H*(I–BP–Ch).

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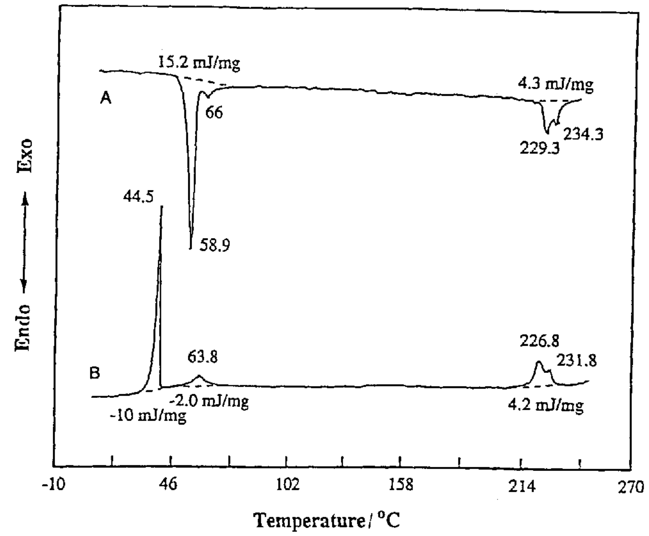


Figure 1. DSC thermogram (10°C min^{-1}) of compound ($n = 3$) MD322A (A) second heating scan; (B) first cooling scan.

corresponds to a weak smectic layer structure. These results correlate with a cholesteric phase. Curve B presents a diffuse reflection at around 5·33 Å, and a sharp first-order reflection at 35·4784 Å which corresponds to strong smectic layers. At this temperature range, results obtained from the optical polarizing micrograph and powder X-ray measurement are both consistent with a smectic A structure. Curves C, D, E reveal that a corresponding decrease occurs in *d*-spacing of first-order small angle reflections from 32·5486 Å to 32·0408 Å, with a subsequent decrease in the measurement temperatures. These results correlate with the formation of S_C^* phase due to the tilt angle of ferroelectric liquid crystal molecules increasing with a decrease in temperatures. For curve F, below the temperature of S_C^* phase, the layer spacing changes back from 32·0408 Å to 32·2869 Å and a fluctuation wide angle reflection appears. The phase is preliminary assigned as a S_x (unidentified) phase.

A comparison of results of the mesomorphic ranges of series MD*n*22A with series MD*n*12A ($n = 0, 1, 2, 3$) is summarized in table 2. This table reveals that the mesomorphism of the two series is similar. The MD122A and MD322A compounds have a tendency to form a more ordered smectic phase (S_x) due to a more rigid mesogenic core (biphenyl biphenyl carboxylate) than mesogens with a three phenyl ring ester cores. Moreover, the additional phenyl ring in the mesogenic group of series MD*n*22A results in another mesomorphic phenomena as follows: (i) the total mesophase temperature range widens about 50–80°C compared to the related series MD*n*12A, with the widest mesophasic temperature range being about 210°C, for MD122A; (ii) the ΔS_C^*, ΔCh, ΔTGB_A, and ΔBP seem to remain unaffected. However, the short derivative MD122A has no S_C^* phase. This observation of S_C^* phase depression for MD112A could be accounted for by the fact that the short (less flexible) spacer chain is coupled with a more rigid (four phenyl rings) mesogenic core; and (iii) the increase in total mesogenic temperature range is dominated by the formation of a wide smectic A phase range, thereby implying that a rigid segment close to the flexible chain tends to promote a smectic A phase. On the other hand, this observation implies that the chiral smectic C, smectic A and cholesteric phase ranges decrease as the oxyethylene spacer length increases. The presence of twist grain boundary A and blue phases range increases as the oxyethylene spacer length increases. Those results are the same as those in series MD*n*12A [12].

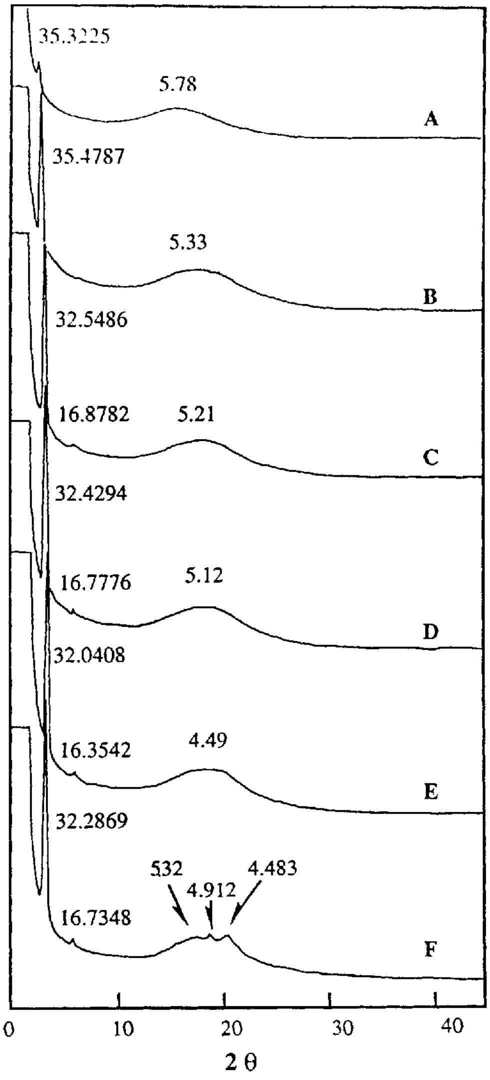
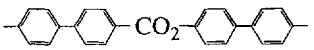
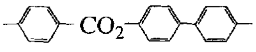


Figure 2. Temperature-dependent X-ray diffraction measurements for MD322A at (A) 226; (B) 180, (C) 130, (D) 120, (E) 102 and (F) 62°C.

Table 2. Mesophase ranges for the series MD*n*22A and MD*n*12A.

Compound	*n*	Mesogenic core†	ΔT_M‡	ΔS_C^*	ΔS_A	ΔTGB_A§	ΔCh	ΔBp§	Reference
MD022A	0	M_{22}	(178·2)§	—	80·2	3	95	—	[this work]
MD122A	1	M_{22}	211	—	147	1·7	28·7	0·1	[this work]
MD222A	2	M_{22}	193·6	91·1	86·2	3·3	12·5	0·5	[this work]
MD322A	3	M_{22}	187·3	75·2	77·5	3·5	3·6	8·2	[this work]
MD012A	0	M_{12}	125·6	—	81·5	—	42	2	[12]
MD112A	1	M_{12}	150·4	91·5	32·7	0·9	17·4	7·9	[12]
MD212A	2	M_{12}	116·9	86·5	15·3	1·6	11·1	2·4	[12]
MD312A	3	M_{12}	111·3	91·3	2·2	3·8	5·5	8·5	[12]

† M_{22} =


M_{12} =


‡ ΔT_M = Total temperature range of mesophase.
§ The values were determined by POM.

This M_{22} series is currently being extended to homologues containing two other chiral tails, (*S*)-2-octanol and (2*S*, 3*S*)-2-chloro-3-methylpentanoic acid, and a range of oxyethylene spacers ($n = 1, 2, 3, 4$). A systematic investigation of their thermal properties is currently underway in our laboratories. Another attempt using polysiloxanes as the polymeric backbone will also be investigated.

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