Journal of Research in Physics Vol. 29, No. 2, 107 - 113 (2003)

Structure - Property Relationship Studies on Chiral Lactic Acid Derivatives

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Received: *February 15, 2002*

Abstract

In earlier studies the mesophase sequences and ferroelectrics characterizations of the H and HO series of lactic acid derivatives were carried out. The chiral centres were connected either by ether or ester groups to the core. The ester linkage of latic acid preferred the formation of the tilted phase since the ethereal connection rather hindered it. These studies were extended to the compounds, which belong to H, HO, M, MO, DM, DMO series.

In this presentation the effect both of lateral methyl substituent and the elongation of the terminal chiral chain by some additional chiral centres will be discussed.

Key words: Ferroelectric liquid crystals, phase sequences, transition temperatures, spontaneous polarization

1. Introduction

Since the first high speed electrooptic device based on ferroelectric liquid crystals (FLC) was discovered [1], a great interest has been directed to a search of new FLC substances which would satisfy application demands. High spontaneous polarization (P_S) together with low viscosity are important properties which can ensure the high switching speed. We have synthesized new FLC materials (H n/m, M n/m, DM n/m) with high value of P_S [2, 3]. Chiral groups used in our study were derived from commercially supplied (S)-(-)-ethyllactate which enables a synthesis of a great number of chiral groups differing in the length of the carbon chain (H n/**, HO n/** [4], M n/**, MO n/**, DMO n/**, DMO n/***).

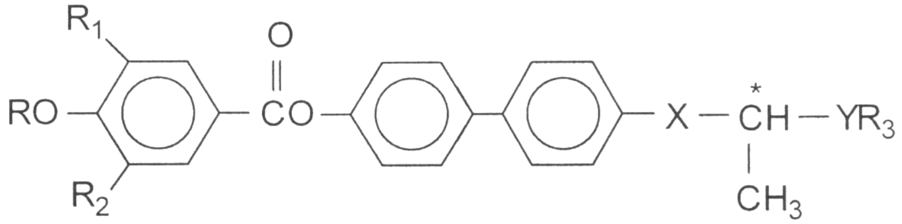

Figure 1. General structural scheme of investigated compounds.

Table 1. List of new ferroelectrics materials.

Series	*R*	R_1	R_2	R_3	*X*	*Y*	Table
H n/m	*n*-alkyl	H	H	*n*-alkyl	OOC	O	2
H n/**	*n*-alkyl	H	H	S-(2)-Me-Bu*	OOC	O	2
M n/m	*n*-alkyl	CH_3	H	*n*-alkyl	OOC	O	3
M n/**	*n*-alkyl	CH_3	H	S-(2)-Me-Bu*	OOC	O	3
MO n/m	*n*-alkyl	CH_3O	H	*n*-alkyl	OOC	O	4
MO n/**	*n*-alkyl	CH_3O	H	S-(2)-Me-Bu*	OOC	O	4
DM n/m	*n*-alkyl	CH_3	CH_3	*n*-alkyl	OOC	O	Fig.2.a-d
BM							5
HO n/m	*n*-alkyl	H	H	*n*-alkyl	O	COO	6
HO n/**	*n*-alkyl	H	H	S-(2)-Me-Bu*	O	COO	6
DMO n/m	*n*-alkyl	CH_3	CH_3	*n*-alkyl	O	COO	7
DMO n/**	*n*-alkyl	CH_3	CH_3	S-(2)-Me-Bu*	O	COO	7

2. Experimental

The sequences of phases and the phase transition temperatures were determined from texture observations by an Amplival Pol-U polarizing microscope equipped with a Boetius hot-stage.

Differential Scanning Calorimetry (DSC) measurements were carried out by a Perkin Elmer DSC7 equipment. The spontaneous polarization (P_S) values were determined from the P(E) hysteresis loop detected during ferroelectric switching in an a.c. electric field at a frequency of 60 Hz.

3. Results

Phase sequences and transition temperatures of the H n/m and H n/** series are shown in Table 2. All substances exhibit a wide temperature range of SmC* phase characterised by high P_S values. Nearly all substances (except six from the H n/m series) exhibit a phase transition from the SmC* to a low temperature smectic phase, which is denoted by SmN. SmN is an orthogonal phase, dechiralization lines disappear at the phase transition; electrooptic switching is not observable.

The phase sequences of the methyl substituted homologous series (M n/m and M n/**) on cooling are summarized in Table 3. The melting temperatures (m.p.), enthalpies, and the P_S values are given too. As shown in Table 2. and Table 3., all phase transition temperatures for the M n/m and M n/** are significantly lower compared to the H n/m and H n/** series. This effect is well known and can be explained in terms of the steric influence of the methyl group on molecular packing.

Table 2. Phase sequences, transition temperatures (°C) and spontaneous polarization P_S (nC/cm^2) at the temperature 5°C below the transition to the SmC* phase for the homologous series H n/m, H n/**.

Comp.			SmC*		SmA*		N*		BP		I_{SO}	P_S
H 6/5	Cr	40	•	127	-		•	150	-		•	64
H 6/7	Cr	37	•	124	-		•	143	-		•	57
H 6/8	Cr	40	•	122	-		•	138	•	139	•	62
H 6/9	Cr	32	•	120	•	126	•	134	•	135	•	57
H 6/10	Cr	40	•	119	•	128	•	132	•	133	•	45
H 6/12	Cr	70	•	119	•	129	•	131	•	133	•	43
H 8/**	SmN	64	•	122	-		•	153	-		•	59
H 8/4	SmN	70	•	138	-		•	163	-		•	62
H 8/5	Cr	72	•	134	-		•	145	-		•	91
H 8/7	Cr	63	•	132	-		•	140	-		•	82
H 8/8	SmN	61	•	128	-		•	134	-		•	60
H 9/8	SmN	57	•	129	-		•	130	•	133	•	95
H 9/9	SmN	67	•	127	-		•	130	•	131	•	88
H 10/**	SmN	72	•	126	-		•	132	•	134	•	77
H 10/5	SmN	75	•	135	-		•	139	-		•	86
H 10/7	SmN	69	•	130	-		•	139	-		•	67
H 10/8	SmN	71	•	133	-		-		-		•	66
H 10/10	SmN	68	•	128	-		-		-		•	61
H 10/12	SmN	75	•	132	-		-		-		•	50
H 12/**	SmN	82	•	142	-		•	157	-		•	32
H 12/4	SmN	79	•	142	-		•	143	-		•	55
H 12/5	SmN	69	•	136	-		-		-		•	59
H 12/7	SmN	81	•	144	-		•	149	-		•	43
H 12/8	SmN	77	•	136	-		-		-		•	59
H 12/10	SmN	64	•	127	-		-		-		•	63

Table 3. Phase sequences, transition temperatures (°C) and spontaneous polarization P_S (nC/cm^2) at a temperature 5°C below the transition to the SmC* phase for the homologous series M n/m, M n/**.

Comp.	m.p.	Cr		SmC*		N*		BP		I_{SO}	P_S
M 6/9	63 [28.5]	•	6	•	77 [2.4]	•	105 [0.7]	-		•	120
M 8/**	46 [15.4]	•	10	•	80 [3.5]	•	87	•	94 [0.8]	•	192
M 8/5	50 [8.3]	•	10 [25.8]	•	89 [3.1]	•		-	104 [1.0]	•	121
M 8/6	65 [23.0]	•	25	•	80 [3.2]	•		-	107 [1.0]	•	180
M 8/10	76 [55.0]	•	34 [36.5]	•		•	76 [3.6]	-		•	
M 10/**	57 [37.4]	•	-10	•	82 [3.2]		89	•	94 [1.0]	•	153
M 10/10	75 [38.3]	•	25 [35.0]	•	89 [4.3]	•	90	•	91 [1.1]	•	83
M 12/6	44 [21.9]	•	25 [32.4]	•	91 [4.1]	•		-	96 [1.1]	•	81
M 12/10	50 [29.5]	•	24 [46.1]	•		-		-	87 [6.1]	•	74

When we compare the properties of the M n/m compounds and their MO n/m analogues, a significant difference can be observed: the SmC* - Cr phase transitions of the M n/m series are lowered substantially and the transitions to the isotropic state are shifted to slightly higher temperatures (Table 3. and Table 4.). The narrow blue phase (BP), which appears for the M n/m series is not observable for the MO n/m series.

A comparison of the P_S values for MO n/m and H n/m (Table 4. and Table 2.) shows that the methoxy group does not influence the P_S value.

Table 4. Phase sequences, transition temperatures (°C) and spontaneous polarization P_S (nC/cm^2) at the temperature 5°C below the transition to the SmC* phase for the homologous series MO n/m, MO n/**.

Comp.			SmC*		SmA		N*		BP	I_{SO}	P_S
MO 8/5	Cr	54	●	69	●	79	●	80	-	●	66
MO 8/7	Cr	37	●	82	-		●	103	-	●	50
MO 8/12	Cr	37	●	65	-		●	85	-	●	24
MO 10/**	Cr	55	●	71	●	77			-	●	66
MO 10/5	Cr	62	●	81	-		-		-	●	57
MO 10/10	Cr	45	●	89	-		-		-	●	57
MO 10/12	Cr	61	●	80	-		-		-	●	35
MO 12/5	Cr	70	●	82	●	85	-		-	●	27
MO 12/7	Cr	52	●	86	-		-		-	●	61
MO 12/8	Cr	66	●	80	●	85	●	87	-	●	47
MO 12/10	Cr	49	●	85	-		-			●	76
MO 12/12	Cr	62	●	82	-		-		-	●	66

The data of the DM n/m series [5], measured by DSC, were in good accordance with that of the microscopic observations. The phase diagrams of four homologous series of DM n/m can be seen in Fig.2a-d. Almost every member of the homologous series exhibits monotropic BP, N*, SmC* mesophases, except DM 10/6, which has a very short enantiotropic N* phase (Fig.2c).

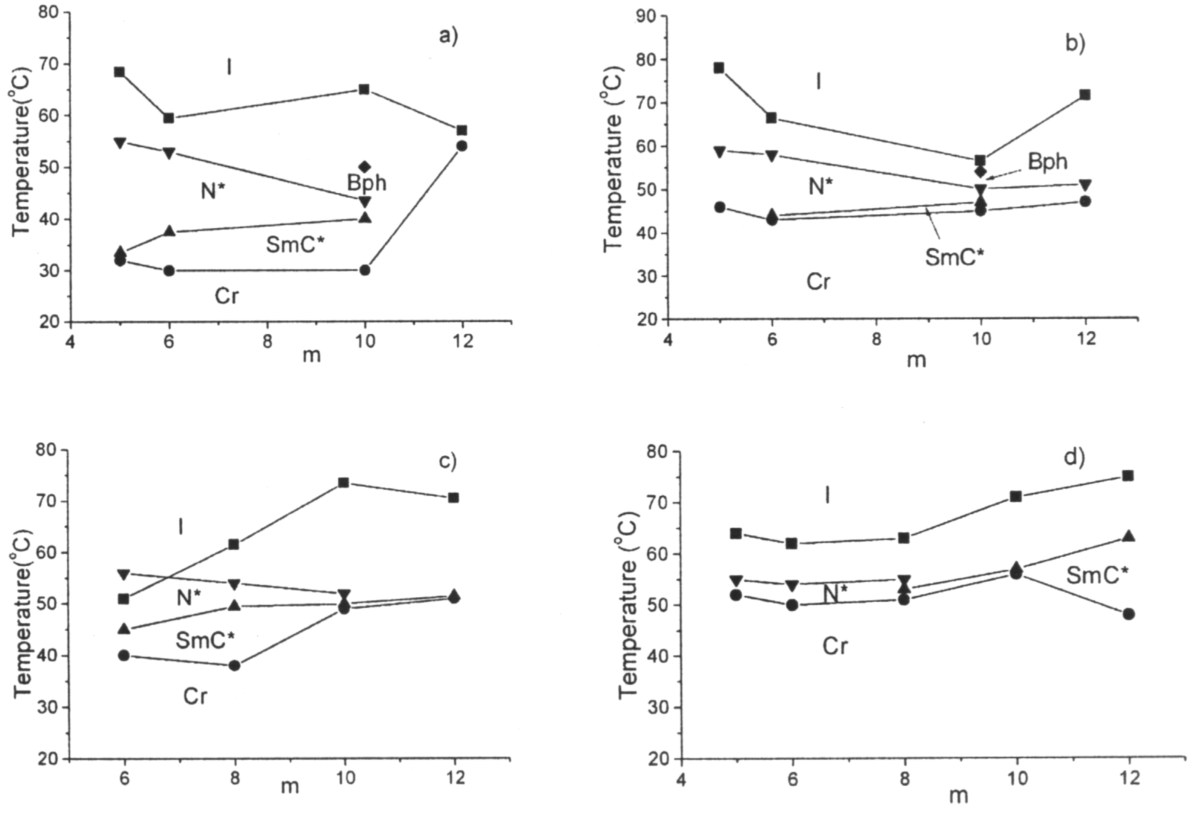

Figure 2a-d. Phase diagrams of the homologous series a) DM 7/m, b) DM 8/m, c) DM 10/m, d) DM 12/m .

Binary mixtures of these compounds were prepared and investigated (Table 5). The mixtures (BM1-BM6) were composed of members of the DM n/m series with chiral chains differing from each other by four carbon atoms in length. These mixtures exhibit the enantiotropic SmC* and N* phase. Presumably the intercalated tail-to-tail packing of the molecules stabilizes the ferroelectric phase, making it enantiotropic.

Table 5. Phase sequences and transition temperatures (°C) for the binary mixtures.

Mixtures	Comp.	Wt[%]	m.p.	Cr	SmC*	N*	I
BM1	DM7/6	50	46.5	• (30)	• 51	-	•
	DM7/10	50					
BM2	DM10/8	60	45	• (38)	• 48	• 53.5	•
	DM10/12	40					
BM3	DM10/8	46.7	45	• (37)	• 49	• 53	•
	DM10/12	53.3					
BM4	DM12/8	44.1	50	• (37)	• 54	• 55	•
	DM12/12	45.9					
BM5	DM12/8	43.2	52	• (40)	• 54	-	•
	DM12/12	56.8					
BM6	DM12/8	40	54	• (40)	• 55	-	•
	DM12/12	60					
BM7	DM10/8	33.3	78	• (55)	• (72)	-	•
	M8/10	66.7					
BM8	DM8/10	50	57	• (40)	• (55.5)	• 59	•
	M8/10	50					
BM9	DM7/5	60	51	• (28)	• (36)	• 51	•
	DM12/12	40					
BM10	DM7/5	40	52	• (40)	• (42)	• 52	•
	DM12/12	60					
	M8/10	100	76	• (34)	• 76	-	•

The phase sequences of two series of chiral liquid crystalline substances HO n/m, having an function as connecting group, are shown in Table 6. All compounds exhibit BP, N* and SmA* phases. The ferroelectric SmC* phase disappears.

Table 6. Phase sequences and transition temperatures (°C) for the homologous series HO n/m and HO n/**.

Comp.	Cr		SmB		SmC*		SmA*		N*		BP		Iso
HO 8/6	•	32	•	43	-		•	52	•	95	•	98	•
HO 8/**	•	40	•	56	-		•	66	•	82	•	85	•
HO 9/6	•	33	•	42	-		•	53	•	87	•	91	•
HO 10/6	•	27	•	44	-		•	64	•	92	•	95	•
HO 10/8	•	39	•	42	-		•	55	•	84	•	87	•
HO 10/10	•	37	•	40	-		•	61	•	77	•	83	•
HO 10/12	•	36	•	40	-		•	59	•	77	•	83	•
HO 10/**	•	41	•	53	•	58	•	65	•	84	•	87	•

Two new chiral homologous series of DMO n/m were synthesized (Fig. 3) and characterised too.

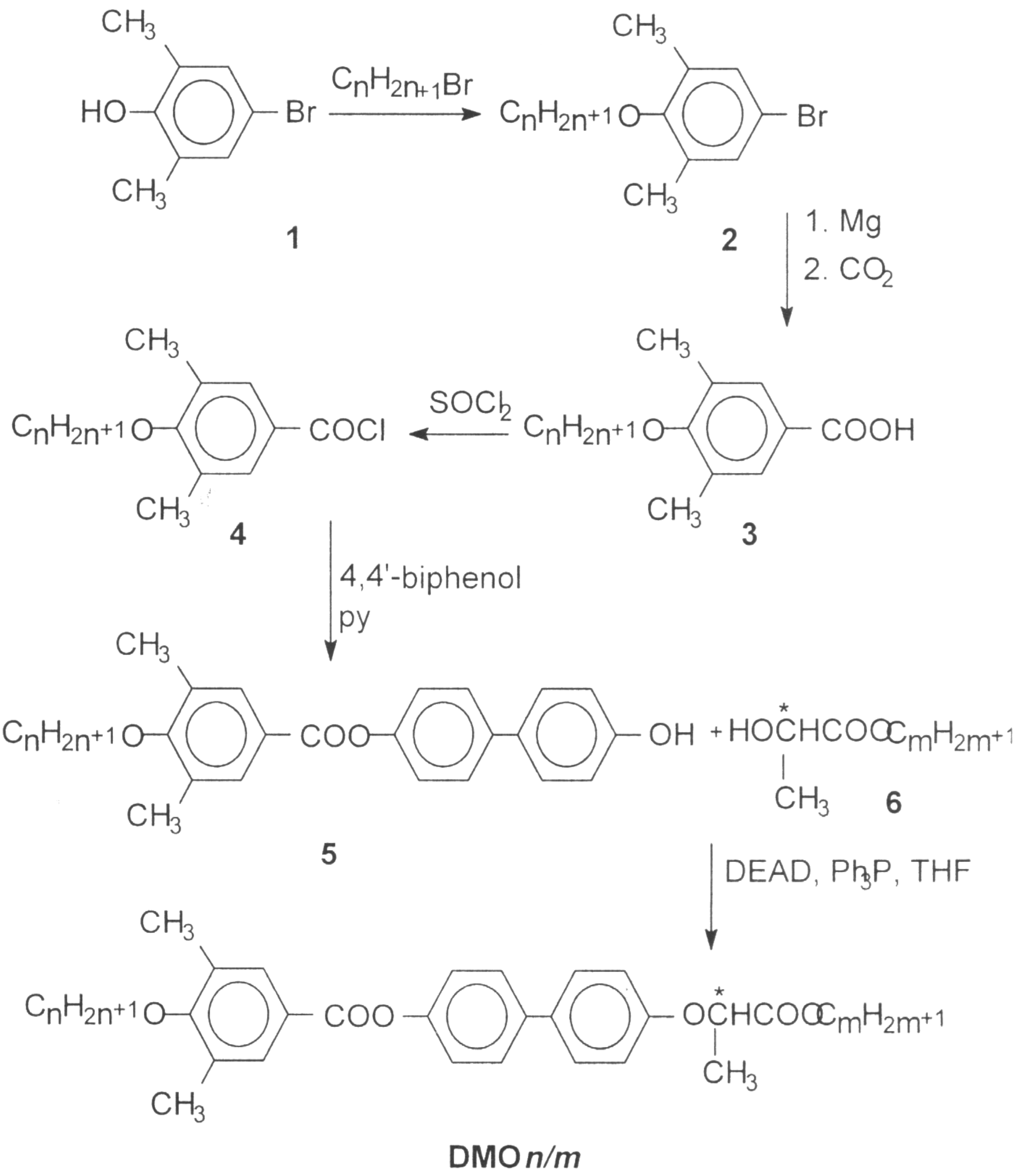

Figure 3. Synthesis of DMO n/m series.

These materials do not possess any liquid crystalline phase (Table 7). Having low melting points, these new materials can be used as chiral additives to decrease the melting points of multicomponent ferroelectric mixtures.

Table 7. Melting temperatures (°C) for the homologous series DMO n/m, DMO 12/** and DMO 12/***.

Comp.	m.p.	I
DMO 10/6	35-38	•
DMO 10/10	53-54.5	•
DMO 10/12	44.5-46.5	•
DMO 12/10	52-53	•
DMO 12/12	52-54	•
DMO 12/**	30-32	•
DMO 12/***	Liquid at -20	

4. Conclusion

In the non-substituted series (H n/m), where the chiral center is connected to the core by an ester function, the mesophase formation is enhanced, the ferroelectric SmC* phase has a wide temperature range. This fact is due to the conjugation between the aromatic system and the carbonyl group of the chiral part, since the core of the molecule is enlarged and the in-plane conformation is more favourable.

The methyl or methoxy substituent in position 3 of the phenyl ring (M n/m and MO n/m series), decreases the transition temperatures in comparison to the non-substituted derivatives (H n/m series).

The introduction of two methyl groups into 3,5-positions gives rise to a dramatic change of mesogenic behaviour. The members of the DM n/m series show only monotropic mesophases. The ether linkage of the chiral center hinders the formation of ferroelectric properties (HO n/m), the rigid core of the molecule becomes shorter and it is enough to destroy completely the liquid crystalline behaviour in DMO n/m series.

The introduction of the second chiral center enlarges the molecule, i.e. the elongation of the chiral part, results in a higher value of P_S (M 10/** and MO 10/**).

These effects suggest that the most powerful compounds are the H n/m, M n/m and MO n/m series which have a wide SmC* range and a high value of P_S.

Acknowledgments

This work was supported by Grants No. 202/99/1120 and No. 202/00/P044 of the Grant Agency of the Czech Republic and by the Hungarian Research Fund OTKA T032667, T030401 and T022772.

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