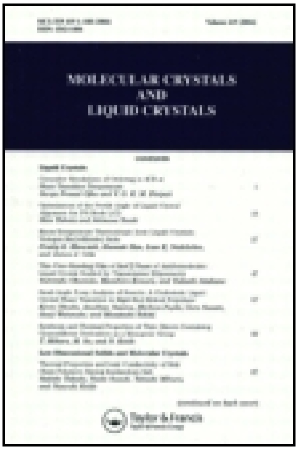

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FERROELECTRIC S_C^* PHASE IN SOME BENZOATE SERIES*

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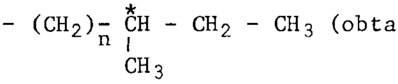
Abstract Several homologous benzoate series which exhibit ferroelectric smectic S_C^* phases have been synthesized. The used chiral acid chains were prepared from commercially available α-amino acids. The series allow us to determine the influence of the size of the substituent of the chiral carbon on the existence and the stability of the S_C^* phase. They also give some compounds or mixtures which display high spontaneous polarization.

INTRODUCTION

Since the discovery of ferroelectricity in chiral smectic S_C^* phase by R. Meyer et al[1] in 1975 and the proposal of various types of electro-optic devices with a high response speed[2,3], the search of new ferroelectric liquid crystals was accelerated. Several phenyl benzoate and cinnamate series with classical chains  $-(CH_2)_n-\overset{*}{C}H(CH_3)-CH_2-CH_3$ (obtained from the commercially available (S)(-)2-methyl-1-butanol) have been reported[4-10]. Recently K. Yoshino et al[11], C. Bahr et al[12] and G. Anderson et al[13] have reported the biphenyl and benzoate series with the chiral chains obtained from the optically active α-amino acids. These compounds display a high spontaneous polarization. In order to obtain other materials with

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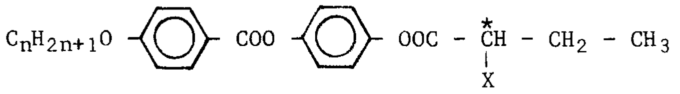
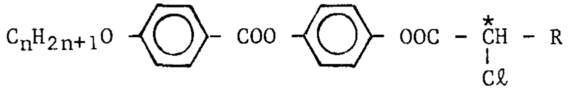
this property and to study the influence of the substituent size and polarity on the chiral carbon atom on the existence and the stability of the S_C^* phase, we have synthesized two chiral series which belong to the general formulae :

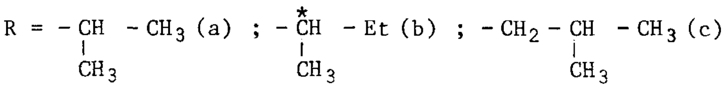


I

and 

II

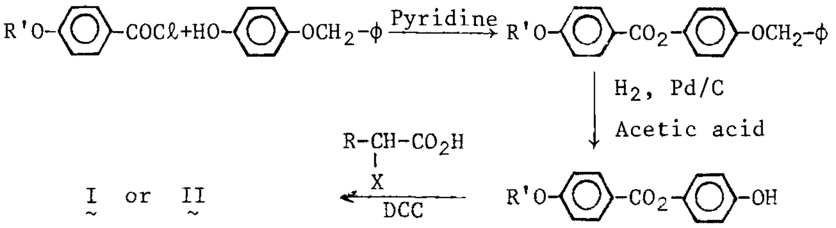
where X = $-CH_3$, $-C\ell$, $-Br$



$$R = -\underset{CH_3}{CH}-CH_3\ (a)\ ;\ -\overset{*}{\underset{CH_3}{CH}}-Et\ (b)\ ;\ -CH_2-\underset{CH_3}{CH}-CH_3\ (c)$$

RESULTATS AND DISCUSSION

The compounds of the two series I and II were prepared following the scheme :

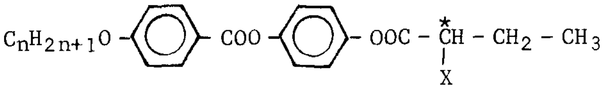


where R' = C_nH_{2n+1}

The acids $R-\overset{*}{\underset{X}{CH}}-COOH$ with X = $C\ell$, Br were obtained from the corresponding α-amino acids at first with concentrated HNO_3 and then with concentrated $HC\ell$ or HBr.

All the compounds were purified by chromatography on silica gel with toluene as eluent and recrystallized from absolute ethanol. They are mesogenic and most of them exhibit the ferroelectric smectic C^* phase. The transition temperatures were determined both by microscopic observation and DSC measurements. The structure of the mesophases was identified by their textures and by contact method.

Series I



I

The transition temperatures and mesomorphic properties of compounds I are listed in Table I

TABLE I Transition temperatures (°C) of compounds I

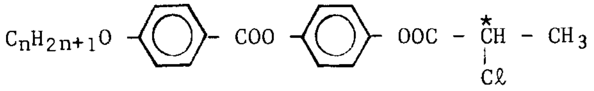
n	X	K	S_H*	S_G*	S_C*	S_A	N*	I
9	CH_3	. 49	-	-	(. 46)	. 53	-	.
12	CH_3	. 53	-	-	(. 52)	. 60	-	.
10	Cℓ	. 48	(. 36)	. 53	-	. 77	-	.
12	Cℓ	. 52	(. 42)	. 53	-	. 79.5	-	.
9	Br	. 66	-	-	(. 48.5)	(. 60)	(. 63)	.
12	Br	. 74.5	-	-	(. 44)	(. 70)	-	.

The meaning of the signs used in this Table and the following are :

K : crystal phase
S : smectic phase A, C*,...
N* : cholesteric phase
I : isotropic phase

. = the phase exists
\- = the phase is not observed
( ) = monotropic phase

With the small size X = Cℓ, the mesomorphic range of the compounds is higher than that with X = CH_3 or Br. On the other hand, these derivatives do not exhibit the ferroelectric S_C* phase but they display the S_A phase and the more ordered smectic phases (S_G* and S_H*). With the short chiral chain, the derivatives having the formula :


III

n = 9 K 92 (S_A 84) I

n = 12 K 89 (S_A 80) I

also do not show the S_C^* phase and the S_A phase is only metastable.

When X = CH_3 having roughly the same size than that of chlorine, the mesomorphic range is shorter but one can observe the existence of the S_C^* phase. With the biggest size X = Br, the observed mesophases (S_A, S_C^* and/or N^*) are only metastable.

Then with the series I, we must point out that :

- the clearing point increases with the polarity of X
- the mesomorphic range decreases with the size of X
- the existence of S_C^* phase is depressed with the small size and the high polarity of X

<u>Series II</u>

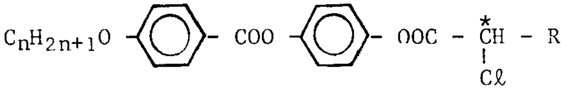

II

Table II gives the transition temperatures and mesomorphic properties. Most of these compounds display the metastable ferroelectric S_C^* phase. The difference on the molecular structure between these derivatives and those of series I (X = Cℓ) lies in the steric hindrance of the group R which :

- favors the existence of the S_C^* phase
- decreases the mesomorphic range
- increases the spontaneous polarization because the polarity of Cℓ is high and this steric hindrance prevents the free rotation round the bonding of chiral carbon atom and that of - COO -.

TABLE II Transition temperatures (°C) of compounds II

n	R	K	S_C^*	S_A	N^*	B_P	I
9	a	. 67	(. 45)	(. 61)	-	-	.
12	a	. 68	(. 44)	(. 67)	-	-	.
8	b	. 69.5	-	(. 48.4)	(. 48.6)	(. 49.3)	.
9	b	. 64	(. 34)	(. 50)	-	-	.
10	b	. 66	(. 36)	(. 53)	-	-	.
11	b	. 69	(. 38)	(. 54.5)	-	-	.
12	b	. 62	(. 38)	(. 57)	-	-	.
13	b	. 52	(. 39)	. 59	-	-	.
6	c	. 80	-	-	-	-	.
7	c	. 57	-	(. 48)	-	-	.
8	c	. 62.5	-	(. 51)	-	-	.
9	c	. 59	(. 35)	(. 50)	-	-	.
10	c	. 48.5	(. 35)	. 53.5	-	-	.
11	c	. 58	-	(. 52.5)	-	-	.
12	c	. 51.5	(. 40)	. 55	-	-	.
13	c	. 66	-	(. 54)	-	-	.

Some physical properties of the mixtures of the compounds I and II are listed in Table III.

TABLE III Physical properties of some mixtures of compounds I and II (V = ± 10V, e = 1μ)

Mixtures	Polarization (nC/cm^2)	Resp. time (μs)	T (°C)	θ (o)
I (X = CH_3)	- 14	6	33	11
IIa	- 103	43	25	20
IIb	- 104	38	34	14
IIc	- 60	27	35	15

It is clear that the spontaneous polarization of the mixture I ($X = CH_3$) is weak because the chiral carbon atom is weakly polar and there is a free rotation round the bonding of this carbon and that of $-COO-$. The response time of this mixture is very quick (6µs) near the transition $S_C^* - S_A$. The other spontaneous polarizations are high because the chiral carbon atom is lied to the chlorine atom and the steric hindrance of R prevents the free rotation round the preceding bonding.

Finally let us point out the uncommon behaviour observed on heating and on cooling with the compound IIb (n = 8), all the mesophases of which are metastable. On cooling from the isotropic phase, one can observe a blue phase with blue or green polygones. On further cooling the S_A phase with focal conic and homeotropic textures appears.

$$\begin{tikzcd}
I \arrow[r, shift left, "49.1"] & B.P \arrow[l, shift left, "49.3"] \arrow[rr, "48.3"] & & S_A \arrow[dl, "48.4"] \\
 & & N^* \arrow[ul, "48.6"] &
\end{tikzcd}$$

Then on heating from the S_A phase, the cholesteric phase N^* with "finger prints" appears and over this phase, the blue phase becomes visible through a blue polygone texture. This microscopic observation is confirmed by DSC measurements (Figure 1a, b). One can explain this fact as follows : all the observed mesophases are metastable and the blue phase is a crystalline phase. There is a supercooling phenomenon and at 48.3° the N^* phase does not exist, one can only observe the S_A phase.

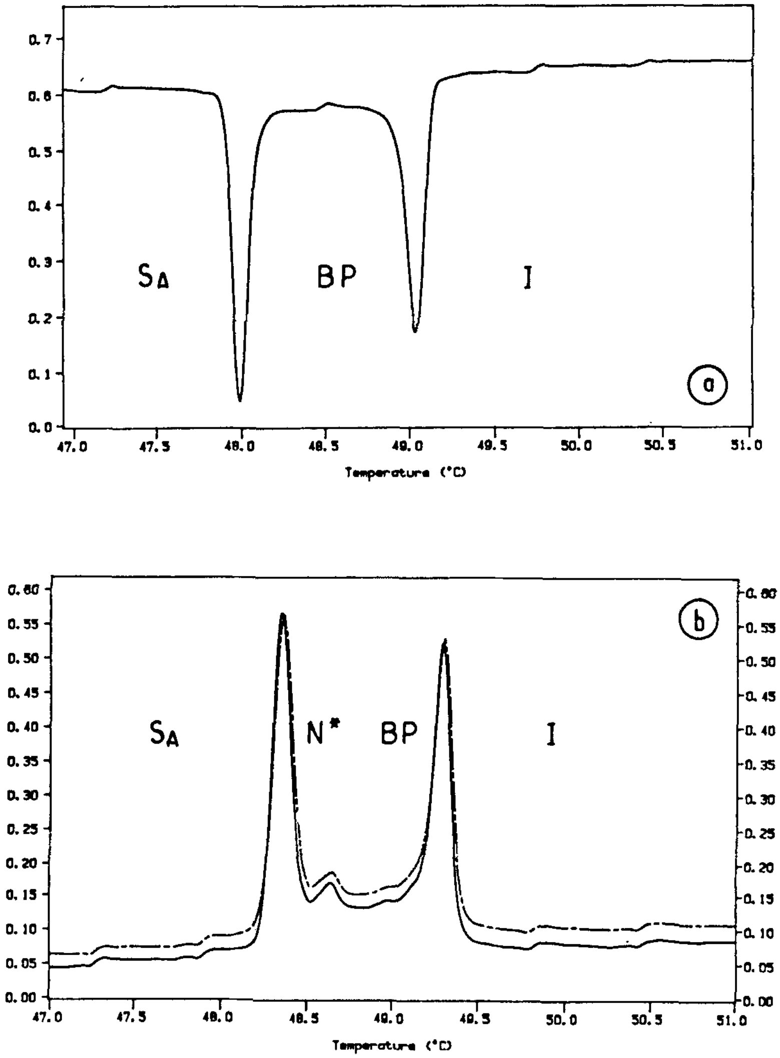


FIGURE 1 a. On cooling from the isotropic phase
b. On heating from the S_A phase

CONCLUSION

With these two benzoate series, we obtain several ferroelectric materials which display a high spontaneous polarization. They provide some new materials for room temperature mixtures and they allow us to determine the influence of the size and the polarity of the chiral carbon atom on the existence of the ferroelectric smectic C^* phase.

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