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Novel Ferroelectric Liquid Crystals Incorporating a Lateral Long-Alkoxy Group

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Syntheses and thermal properties of 4-octyloxyphenyl 4-[3,4-di(2-methylalkanoyloxy)benzoyloxy]-benzoates (**1**) and 4-[3,4-di(2-methylalkanoyloxy)benzoyloxy]phenyl 4-octyloxybenzoates (**2**) are reported. Higher members of compound **1** show chiral smectic C phase as well as cholesteric one, and compound **2** shows only cholesteric one. Both cholesteric and chiral smectic C phases are miscible with those of usual lath-shape liquid crystals, but these show only a fine-particle texture. The effect of the lateral long alkyl group on the mesomorphic properties is discussed.

Keywords: synthesis, ferroelectric LC, long-alkoxy group

INTRODUCTION

In previous papers,^{1–3} we reported that some compounds having a long alkoxy or a long alkoxyphenyl group show mesomorphic properties in spite of the unusual molecular structures. Their molecular structures and mesomorphisms are shown below.

Compound **3** would have a typical lath-like shape, and shows the mesomorphism of an S_C-S_A-N-I type. The related compound **4** having two alkoxy groups at meta-position is non-mesogenic, probably due to rotational isomerization of the groups. Interestingly, compounds **5**, **6** and **7** having a lateral alkoxy group have mesomorphic properties, and that the N-I transition temperature is considerably high. We are interested in the formation of the smectic C phase for compound **5**.

In this paper, we describe the syntheses and thermal properties of the related compounds of **5**, where two 2-methylalkanoate groups are introduced at positions 3 and 4 of the left-side ring.

Compound	Molecular structure	Mesomorphism
3	$C_nH_{2n+1}O-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_nH_{2n+1}$	S _C -S _A -N-I
4	$C_nH_{2n+1}O-\text{C}_6\text{H}_3(\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_nH_{2n+1})$	non-mesogenic

Compound	Molecular structure	Mesomorphism
<u>5</u>	$\begin{array}{c} \text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1} \\ \\ \text{C}_n\text{H}_{2n+1}\text{O} \end{array}$	$\text{S}_\text{C}-\text{N}-\text{I}$
<u>6</u>	$\begin{array}{c} \text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1} \\ \\ \text{OC}_n\text{H}_{2n+1} \end{array}$	$\text{N}-\text{I}$
<u>7</u>	$\begin{array}{c} \text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{OC}_n\text{H}_{2n+1} \\ \\ \text{C}_n\text{H}_{2n+1}\text{O}-\text{C}_6\text{H}_4-\text{COO} \end{array}$	$\text{N}-\text{I}$

EXPERIMENTAL

Compounds 1 and 2 were prepared according to SYNTHETIC SCHEME, where all 2-methylalkanoic acids have S-configuration.

RESULTS

Transition temperatures were determined by using a Mettler FP-52 heating stage fitted with a Nikon POH polarizing microscope, and the results are summarized in Table I.

All the derivatives are mesomorphic, though the mesophase-isotropic transition temperatures are low. The decanoate derivative of 1 shows an S phase as well as Ch one on the cooling stage, where the formation of the S phase results in a rapid recrystallization. The Ch and S phases show a fine-particle texture and no usual focal conic and fan textures. Identification of the mesophases was carried by examination of binary phase diagrams, and the results are shown in Figure 1. In Figure 1a, both mesophases are miscible with Ch and S_C^* phases of the reference compound, and the Ch-I and $\text{S}_\text{C}^*-\text{Ch}$ transitions show a linear correlation against the molar concentration of each component. The dodecanoate derivative of 1 shows only Ch phase, and the extrapolated $\text{S}_\text{C}^*-\text{Ch}$ transition temperature is ca. 10°C.

All derivatives of compound 2 form only Ch phase on the cooling stage, and the formation resulted in a rapid recrystallization. Therefore, the correct transition temperatures were determined by extrapolation from the binary phase diagrams. The example is shown in Figure 1b. We could not observe any smectic phase in the binary mixtures. Therefore, it can be concluded that compound 2 is difficult to form the S_C phase.

The Ch-I transition temperatures of the present compounds are almost independent of orientation of the ester group, and are lower by ca. 60°C than those of compound 5. Probably, steric hindrance between the substituents at positions 3 and 4, especially in the ester groups, is too large for both alkyl groups to arrange parallel. Further examination is now underway.

SYNTHETIC SCHEME

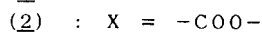
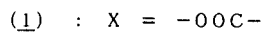
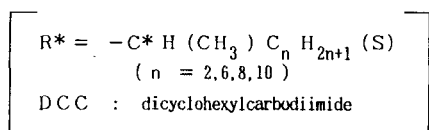
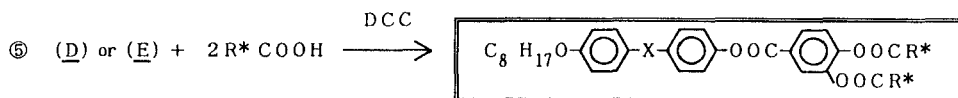
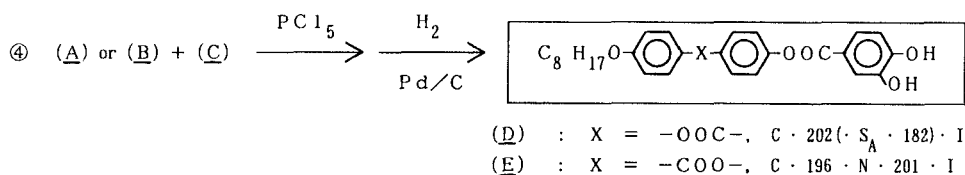
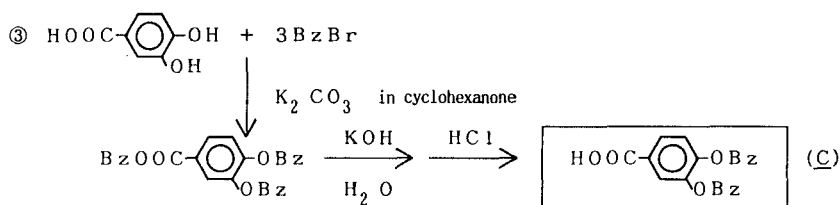
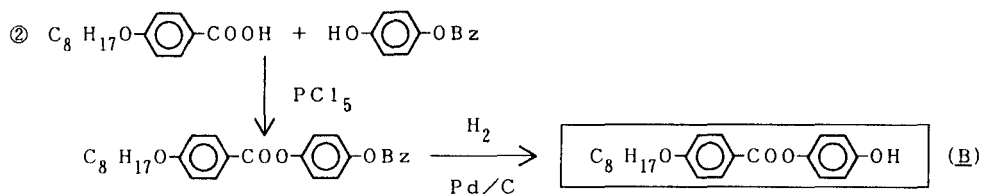
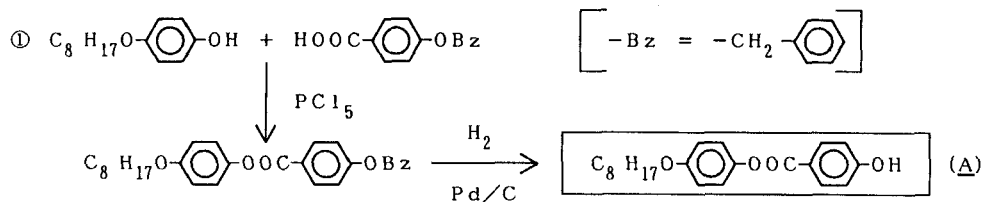
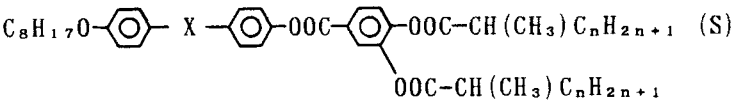


TABLE I
Transition temperatures for compounds 1 and 2 ($T/^{\circ}\text{C}$)



n	Compound <u>1</u> (X= -OOC-)				Compound <u>2</u> (X=-COO-)		
	C	S _C [*]	Ch	I	C	Ch	I
2	· 64	-	(· 45)	·	· 67	(· 48)	·
6	· 40	-	(· 30)	·	· 54	(· 40)	·
8	· 41	(· 5	· 33)	·	· 53	(· 39)	·
10	· 43	[· 10]	(· 34)	·	· 55	(· 41)	·

Parentheses and brackets indicate monotropic and virtual transition temperatures, respectively.

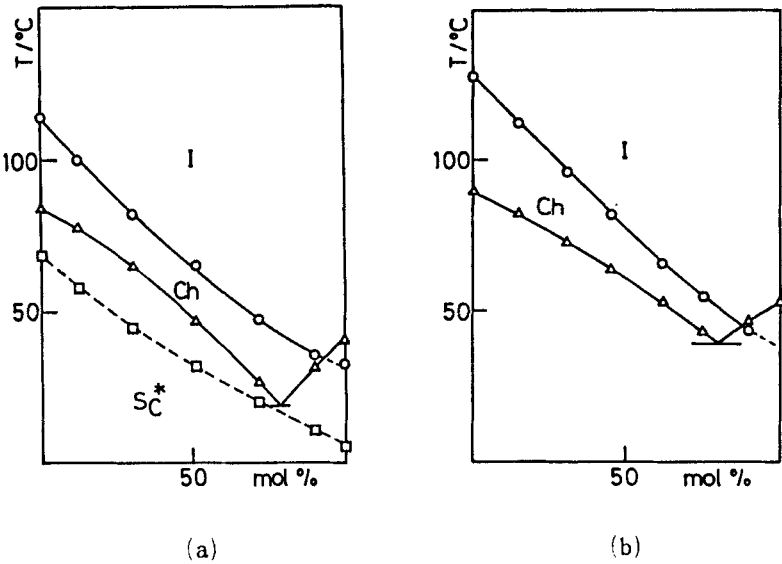


FIGURE 1 Binary phase diagrams for the mixtures of: (a), the decanoate derivative of 1 (on right) and 4-octyloxyphenyl (R)-4-[4-(1-methyl)heptyloxybenzoyloxy]benzoate (on left); (b), the decanoate derivative of 2 (on right) and 4-(4-octyloxybenzoyloxy)phenyl (R)-4-(1-methyl)heptyloxybenzoate (on left). Dashed lines indicate monotropic transition.

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