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Smectic Properties of 4-(4-Alkoxyphenoxycarbonyl)phenyl 4-Formylbenzoates

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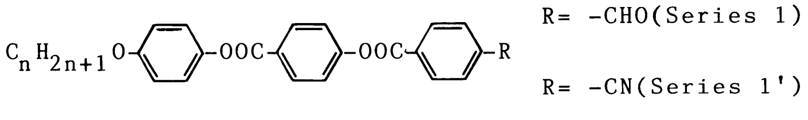
The octyloxy homolog and the higher members of 4-(4-alkoxyphenoxycarbonyl)phenyl 4-formylbenzoates show two kinds of smectic A phases and experience a smectic A-smectic A transition, where the lower smectic A phase has a bilayer arrangement of the molecules, and the upper probably a monolayer one.

It has been known that many liquid crystals having a nitro or a cyano group form four kinds of smectic A phases(monolayer(S_{A1}), bilayer(S_{A2}), partially bilayer(S_{Ad}) and antiphase($S_{\tilde{A}}$)), and show very interesting polymesomorphisms involving a smectic A-smectic A transition and a reentrant phenomenon.[1] The smectic diversity has been frequently discussed in terms of attractive interactions involving dipoles arising from the linkages and terminal polar groups. We are interested in the mesomorphic properties of liquid crystals incorporating a formyl group instead of the cyano and nitro groups, where the dipole moment of benzaldehyde(2.77 D) is smaller than those of benzonitrile(4.40 D) and nitrobenzene(4.2 D).[2]

In this paper, we describe the thermal properties of a homologous series of 4-(4-alkoxyphenoxycarbonyl)phenyl 4-formylbenzoates. The homologous series was prepared according to a similar method described in an earlier paper.[3]



$C_nH_{2n+1}O-C_6H_4-OOC-C_6H_4-OOC-C_6H_4-R$

R= -CHO(Series 1)
R= -CN(Series 1')

(n = 5 - 10)

The phase transitions and thermal properties were examined by using a Nikon Model POH polarizing microscope fitted with a Mettler FP-52 heating stage and a Daini-seikosha SSC-560 differential scanning calorimeter, respectively.

Table 1. Transition temperatures and latent heats for series 1(T/°C)

Carbon number	Series 1								Series 1'			
n	C$^{a)}$	S$_A$	S$_A$	N	I$^{c)}$	ΔH$_{S_A-S_A}$	ΔH$_{S_A-N}$	ΔH$_{N-I}$	S$_{A2}$	S$_{Ad}$	N	I
5	. 129	-	-	. 241	.	-	-	0.5				
6	. 127	. d)	-	. 233	.		-	0.2				
7	. 127	. 144	-	. 227	.	0.2	-	0.4				
8	. 126	. 145	. 167	. 226	.	0	0	0.4	. 175	. 180	. 250	.
9	. 127	. 146	. 188	. 226	.	0.1	0.1	0.4	. 178	. 199	. 240	.
10	. 126	. 151	. 202	. 225	.	0.1	0.1	0.5	. 180	. 214	. 235	.

a) C, S$_A$, N, and I abbreviate crystal, smectic A, nematic, and isotropic solution, respectively. ΔH indicates the latent heats(kJ/mol) for the transitions. b) The transition temperatures were roughly estimated from Fig. 1 in Ref. 4. c) The transition temperatures may involve a certain extent of error since these compounds rapidly decomposed above 200 °C. d) The smectic phase could be observed just before solidification on the cooling stage.

The results are summarized in Table 1, where the transition temperatures for 4-(4-alkoxyphenoxycarbonyl)phenyl 4-cyanobenzoates(series 1') are also indicated, for comparison. Series 1 is so unstable that we were unable to evaluate the correct N-I transition temperatures. The decomposition rapidly prodeeds above 200 °C. The X-ray diffraction studies were also impossible by the same reason. The smectic properties commence from the hexyloxy homolog, and the octyloxy homolog and the after members show two kinds of the smectic phases. Both smectic phases show a quite similar fan texture under a homogeneous alignment. The smectic-smectic transitions could be observed as an instability of the texture. The latent heats for the smectic-smectic and smectic-nematic transitions are considerably low even in higher members. The smectic phase of the lower members is miscible with the lower smectic phase of the higher members. In order to characterize the smectic phases, we examined some binary phase diagrams, and the results are shown in Figs. 1 and 2. In Fig. 1, 4-(4-heptyloxyphenoxycarbonyl)phenyl 4-nitrofuran-2-carboxylate was used as a

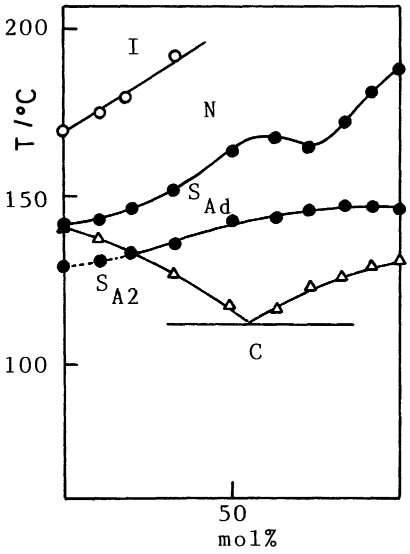


Fig. 1. Binary phase diagram for the mixture of the nonyloxy homolog (on right) and 4-(4-heptyloxyphenoxy carbonyl)phenyl 4-nitrofuran-2-carboxylate(on left).

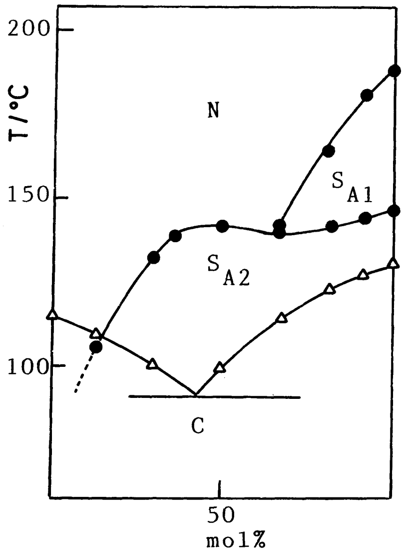


Fig. 2. Binary phase diagram for the mixture of the nonyloxy homolog (on right) and N-[4-(4-heptyloxy-benzoylxoy)benzylidene]-4-cyano-aniline(on left).

standard material, where the upper and lower smectic phases have been assigned to S_{Ad} and S_{A2} phases, respectively.$^{5)}$ In the figure, the lower smectic phase of the nonyloxy homolog is miscible with the S_{A2} phase of the standard material, thereby the S_{A2}-smectic transition shows a linear correlation with the composition of each component. A similar phase diagram was observed in the binary mixture of the nonyloxy homolog and 4-(4-octyloxyphenoxycarbonyl)phenyl 4-cyanobenzoate(series 1'). These results indicate that the lower smectic phase of the present series is assigned to the smectic A phase having a bilayer arrangement of the molecules. Although the upper smectic phase in Fig. 1 has an affinity with the S_{Ad} phase of the standard material, the S_A-N transition shows a maximum at ca. 60 mol% of the nonyloxy homolog and a minimum at ca. 75 mol%. In Fig. 2, N-[4-(4-heptyloxybenzoyloxy)benzylidene]-4-cyanoaniline having intrinsically a S_{Ad} nature was used as a standard material.$^{6)}$ In the figure, the S_A-N transition temperature is steeply depressd by the standard material. These characteristic patterns have been frequently observed in binary mixtures involving polar liquid crystals revealing the S_{Ad} and S_{A1} phases.$^{7)}$ From these results, we can assume that the upper smectic phase of the present series is assigned to the smectic A phase having a monolayer arrangement.

It has been reported that the cyano compounds(series 1') also show two kinds of the S_A phases, where the upper and lower smectic phases are assigned to S_{Ad} and S_{A2} phases, respectively.4) As mentioned above, the dipole moment of the formyl group is smaller than that of the cyano group. Therefore, the difference in the dipolarity around the terminal group is responsible for the diversity of the molecular arrangement in the smectic A phases. We also examined the thermal properties of the related compounds; that is, 4-formylphenyl 4-(4-octyloxybenzoyloxy)benzoate, 4-formylphenyl 4-(4-octyloxyphenoxycarbonyl)benzoate, and 4-(4-octyloxybenzoyloxy)phenyl 4-formylbenzoate. The former two compounds show only a S_{A1} phase, and the last one is non-smetogenic. Recently, Dabrowski et al. reported that a phenylcyclohexane derivative having a terminal formyl group shows the S_{Ad} phase.8)

Consequently, the terminal formyl group is intrinsically able to induce the S_{A2} phase, and the thermal stability is influenced by the gross molecular structure and the electrostatic interactions around the core.

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