

A S_{Ad} - S_{Ad} TRANSITION OF A HOMOLOGOUS SERIES OF 4-CYANOPHENYL
4-(4-ALKOXY-3-BROMOBENZOYLOXY)BENZOATES

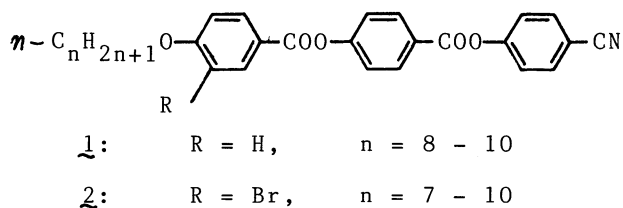
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The thermal properties of some homologs of 4-cyanophenyl 4-(4-alkoxy-3-bromobenzoxy)benzoates have been examined, where the octyloxy homolog shows the reentrant phenomenon of a S_{Ad} - N_{re} - S_{Ad} - N -I type, and the nonyloxy and decyloxy homologs show the mesomorphism of a S_{Ad} - S_{Ad} - N -I type, and experience a S_{Ad} - S_{Ad} transition.

It has been known that liquid crystalline materials having a cyano or a nitro group at the terminal frequently display somewhat interesting mesomorphism such as a reentrance.^{1,2)} A homologous series of 4-cyanophenyl 4-(4-alkoxybenzoxy)benzoates(1) is a typical example.



The nonyloxy homolog of 1 displays the reentrant mesomorphism of a N_{re} - S_{Ad} - N -I type,³⁾ where N_{re} and S_{Ad} represent a reentrant nematic phase and a smectic A phase having a partially bilayer arrangement of the molecules, respectively. Recently, we reported that a binary mixture consisting of N-[4-(4-heptyloxybenzoxy)benzylidene]-4-cyanoaniline and 4-cyanophenyl 4-(4-nonyloxy-3-bromobenzoxy)benzoate displays the reentrant mesomorphism of a $S_A(2)$ - N_{re} - $S_A(1)$ - N -I type, where

the layer spacings for the upper ($S_A(1)$) and lower ($S_A(2)$) phases are 1.16 and 1.26 times of the averaged molecular length of both components, respectively.⁴⁾ These facts indicate that both S_A phases have the partially bilayer arrangement of the molecules (S_{Ad}).

In this paper, we describe the thermal properties of a homologous series of 4-cyanophenyl 4-(4-alkoxy-3-bromobenzoxy)benzoates(2).

Table 1. Transition temperatures($^{\circ}\text{C}$) for the homologous series of 2 and 1

n	C	$S_{Ad}(2)$	N_{re}	$S_{Ad}(1)$	N	I
Compounds <u>2</u>						
7	.	125.6 (- 62.5)	-	-	.	196.8 .
8	.	116.1 (- 72.8)	(. 81.5)	.	136.8 .	186.5 .
9	.	95.7 (- 82.7)	-	.	155.3 .	181.3 .
10	.	96.8 (- 80.7)	-	.	161.6 .	170.9 .
Compounds <u>1</u> ³⁾						
8	.	116 -	-	-	.	229 .
9	.	121 -	(- 116)	.	198 .	229 .
10	.	108 -	(- 95)	.	208 .	222 .

a) The parentheses indicate monotropic transitions. C, S, N, and I represent crystal, smectic, nematic, and isotropic phases, respectively.

The homologs were prepared by a usual method.³⁾ The transition temperatures are shown in Table 1, and are plotted against the carbon number, n in Fig. 1. The thermal stabilities of the N and S_A phases for 2 are less than those for 1, due to an increase in the molecular breadth. However, 2 produce two kinds of S_A phases having a uniaxial nature. As mentioned in a previous paper,⁴⁾ these have the partially bilayer arrangements of the molecules. The $S_{Ad}(1)$ phase has a typical fan texture, and the $S_{Ad}(2)$ phase a considerably broken one. The $S_{Ad}(2)$ phase for the Δ and \circ ; 2, \blacktriangle and \bullet ; 1. heptyloxy homolog shows a typical fan texture.

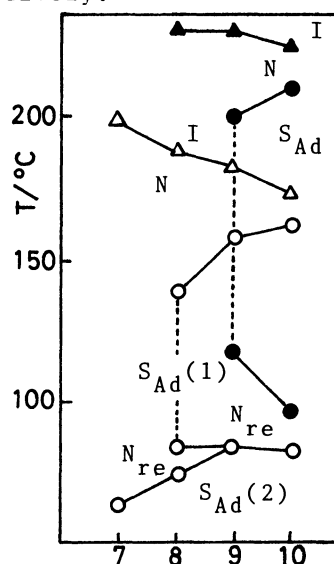
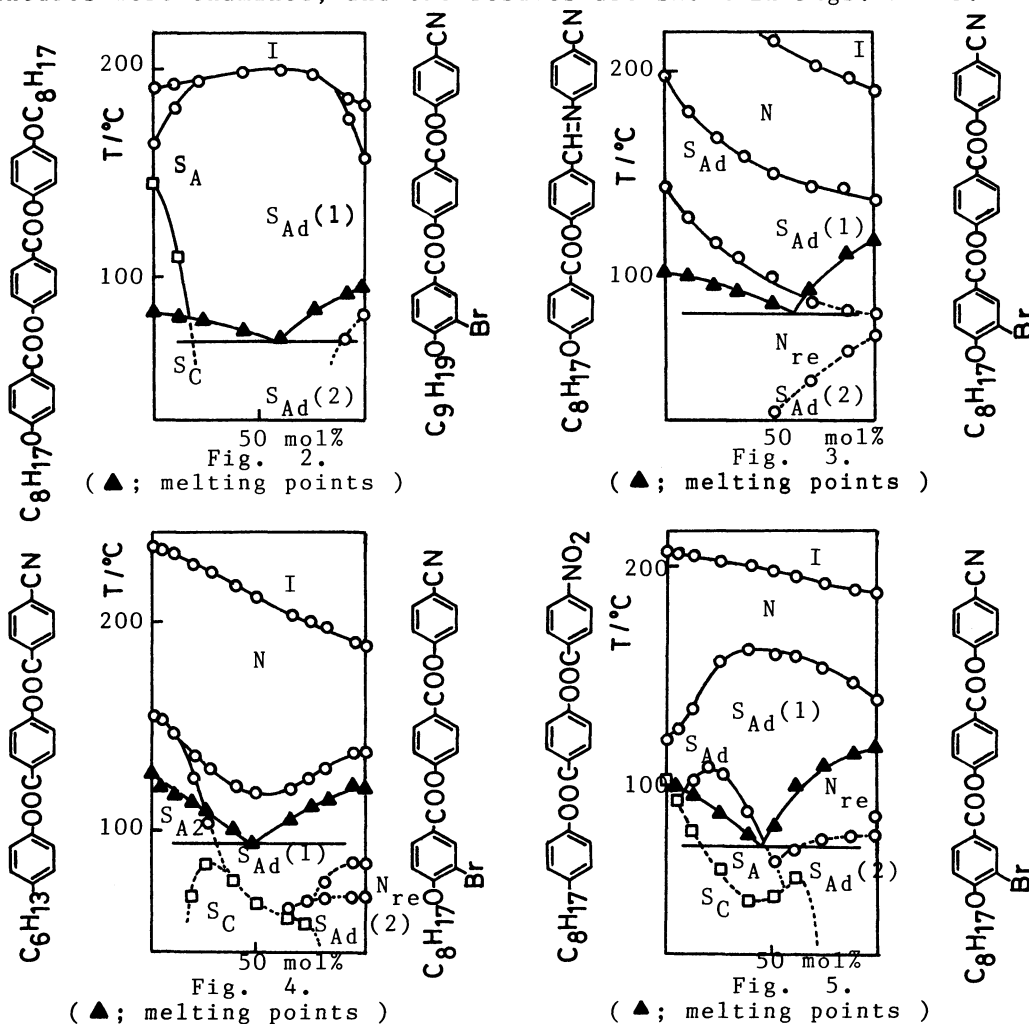


Fig. 1.

The octyloxy homolog shows the reentrant mesomorphism of a $S_{Ad}(2)-N_{re}-S_{Ad}(1)-N-I$ type. The nonyloxy and decyloxy homologs show the mesomorphism of a $S_{Ad}(2)-S_{Ad}(1)-N-I$ type. The heptyloxy homolog shows the mesomorphism of a $S_{Ad}(2)-N-I$ type. The $S_{Ad}-S_{Ad}$ transitions could be easily detected by means of a polarizing microscope fitted with a Mettler FP-5 heating stage. However, the $S_{Ad}-S_{Ad}$ transitions could not be detected by means of a differential scanning calorimeter. We assume that the latent heats for the transitions are less than 50 J/mol. As far as we know, series 2 is the first instance to experience the apparent $S_{Ad}-S_{Ad}$ transitions in a pure state, though Shashidhar et al. have also reported that a binary mixture consisting of 4-nitrophenyl 4-(4-hexyloxybenzoyloxy)benzoate and 4-cyano-4'-(4-nonyloxybenzoyloxy)azobenzene, shows a similar transition, which can be observed by the X-ray measurement.⁵⁾

In order to characterize these S_{Ad} phases, the miscibility diagrams for some binary mixtures were examined, and the results are shown in Figs. 2 - 5.



In Fig. 2, the $S_{Ad}(1)$ phase is isomorphous with the S_A phase of the nonpolar liquid crystal, thereby the S_A -N(I) transition temperatures show a remarkable non-ideal solution behavior. However, the thermal stabilities of both $S_{Ad}(2)$ and S_C phases rapidly decrease with increasing the concentrations of both components. In Fig. 3, the thermal stability of the $S_{Ad}(2)$ phase also decreases with increasing the concentration of the reference compound, while the $S_{Ad}(1)$ phase is well miscible with the S_{Ad} phase of the reference compound. In Fig. 4, both $S_{Ad}(1)$ and $S_{Ad}(2)$ phases are immiscible with the S_{A2} phase of the reference compound, and the diagram shows an injected S_C (probably S_{C2}) phase around the center of the diagram. In Fig. 5, the $S_{Ad}(1)$ phase is miscible with the S_{Ad} phase of the reference compound, though the $S_{Ad}(2)$ phase disappears in the diagram. Some interesting trends are recognized in Figs. 4 and 5. The first is that the S_{Ad} -N transition temperatures show a remarkable upward convexity which usually observed in so-called 'polar - nonpolar' mixtures,^{1,2)} while both components are polar. The second is that the diagram shows an injected S_A phase having a uniaxial nature. This phase is proposed to be an antiphase ($S_{\tilde{A}}$). The third is that the S_C phases also show interesting non-linearities with composition. These interesting phenomena should be concerned with a dipole - dipole interaction of both components.⁶⁾ Further study is now underway.

References

- 1) G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals," Heyden & Son Inc., Philadelphia (1984), p. 134.
- 2) D. Demus, S. Diele, S. Grande, and H. Sackman, "Advances in Liquid Crystals," ed by G. H. Brown, Academic Press, New York (1983), p. 1.
- 3) G. Sigaud, Nguyen Huu Tinh, F. Hardouin, and H. Gasparoux, Mol. Cryst. Liq. Cryst., 69, 81 (1981).
- 4) Y. Nishihata, H. Sakashita, H. Terauchi, S. Takenaka, and S. Kusabayashi, J. Phys. Soc. Jpn., in press.
- 5) R. Shashidhar, B. R. Ratna, and S. K. Prasad, Mol. Cryst. Liq. Cryst., 102, 105 (1984).
- 6) S. Takenaka, M. Koden, and S. Kusabayashi, J. Phys. Chem., in press.

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