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REENTRANT NEMATIC AND SMECTIC C PHASES IN BINARY SYSTEMS OF 4-(β-CYANETHYL)-PHENYL 4-n-ALKYLOXY-CINNAMATES

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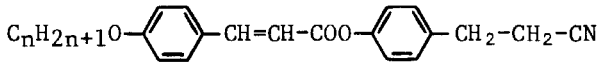
Abstract: In binary systems of 4-(β-cyanethyl)-phenyl 4-*n*-alkyloxycinnamates reentrant nematic and reentrant smectic C phases occur. In three systems studied the phase sequences S_C N_{re} S_A N Is and $S_{C(re)}$ N_{re} S_C S_A N Is were found.

Cladis first observed that binary mixtures of *p*-cyano substituted azomethines[1] and cyanoalkylbiphenyls[2] show the following phase sequence with decreasing temperature: nematic(N), smectic A (S_A) and again nematic. The low temperature nematic phase was called "reentrant" nematic phase (N_{re}). Later on Engelen *et al.*[3] found reentrant nematic phases also in binary mixtures of terminal polar liquid crystals and terminal non-polar liquid crystals. We present first investigations about 4-(β-cyanethyl)-phenyl 4-*n*-alkyloxycinnamates[4] which show a strong tendency to form reentrant phases in binary mixtures. The lower members of this homologous series exhibit nematic phases; the higher homologues possess additional smectic phases (Table 1).

We have studied the diagrams of state of binary systems by means of the contact method[5] and by investigations of singular concentrations. Combining a nematic homologue of the series with a homologue exhibiting S_C S_A or S_C S_A N polymorphism, analogous diagrams were obtained (see Figures 1-3). The common feature of these diagrams is the concave curvature of the S_A-N transition curve and the convex

Table 1



n	Cr		S_C		S_A		N		Is
6	•	64[x]; 71.5	-		-		•	109.2	•
8	•	71.5[x]; 87.2	-		-		•	108.2	•
10	•	68[x]; 72	(•	58)	•	109	•	109.5	•
12	•	73.5[x]; 82	(•	58)	•	117	-		•

Cr solid crystal
S_A, S_C smectic A resp. C
N nematic
Is isotropic liquid

The numbers between the phase symbols are the transition temperatures (°C). Brackets denote metastable phases.

[x]melting points of metastable solid modifications.

curvature of the S_C-N curve with respect to the temperature axis. Comparing the diagrams of state in Figures 1-3, we can derive that the existence range of smectic phases generally increases with increasing chain lengths of the components in the binary system. The complicated shape of the S_A-N and S_C-N curves gives rise to the occurrence of reentrant nematic and reentrant smectic C phases ($S_{C(re)}$).

Additionally to the well known sequence N_{re} S_A N in all diagrams, the unusual sequences S_C N_{re} S_A N and $S_{C(re)}$ N_{re} S_C S_A N were found. The unusual phase sequences occur in a limited concentration range. The S_C range between S_A and N_{re} is relatively small (0,3-3 K). In most cases (except for Figure 3), the $S_{C(re)}$ phase could be detected only by rapid supercooling. Although the textures of the N_{re} and S_C resp. $S_{C(re)}$ phases are not very different, these phases could be distinguished by the different behaviour after mechanical and dielectric deformations. Furthermore, the transitions were clearly indicated by the appearance of a transition front. The phase transitions were examined by

differential scanning calorimetry (DSC2, Perkin-Elmer). In principle, all phase transitions found by optical observations could be detected also by calorimetry, except the transition N_{re}-SC. This is obviously caused by the fact that the SC range between N_{re} and S_A is too small. The order of magnitude of the transition enthalpies is shown in Table 2.

Table 2

Transition	$S_{C(re)}/N_{re}$	N_{re}/S_A	S_C/S_A	S_A/N	N/Is
$\Delta H/Jmol^{-1}$	50	100-300	100-250	500	2800

Because the metastable S_C phases of the pure substances (C_9, C_{10}, C_{12}) crystallize quickly, the X-ray investigations were performed on an equimolar mixture of the C_9 and C_{10} compounds in which the S_C phase could be supercooled about 10 K. According to preliminary measurements the layer spacing d in the S_A as well as S_C phases is distinctly larger than the average length l of the C_9 and C_{10} molecules in its most stretched conformation. The ratio d/l was found to be about 1.14. This behaviour is characteristic of those molecules which possess a strong polar head group (CN) on the one end and a non-polar aliphatic tail on the other end.[6,7] This special molecule structure leads to a kind of bilayer structure with interdigitated molecules in each layer. Finally, it should be noted that the 4-(β-cyanethyl)-phenyl 4-*n*-alkyloxycinnamates form reentrant nematic and smectic phases in binary mixtures with a great number of liquid crystals possessing quite different chemical structures. These results will be published elsewhere.

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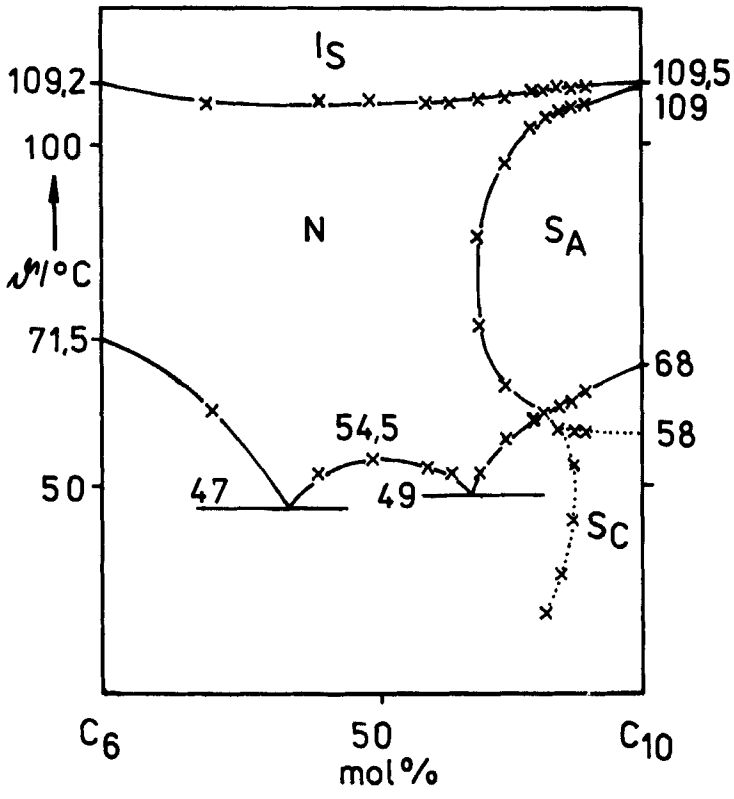

FIGURE 1

NOTE: *In each of the figures, the melting curve drawn relates to that solid modification which was obtained in a large concentration range. The dotted curves indicate phase transitions in the supercooled state.*

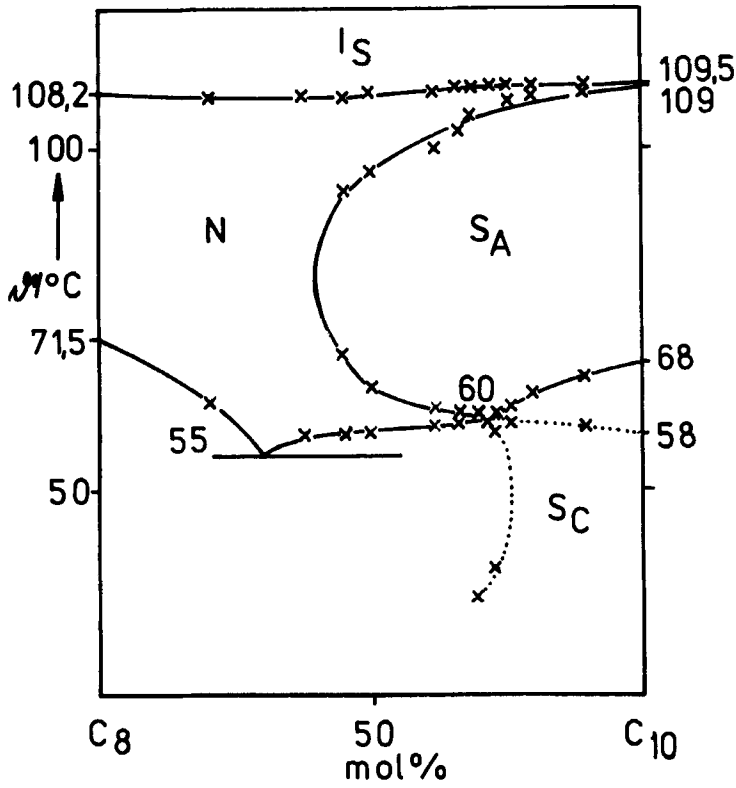

FIGURE 2

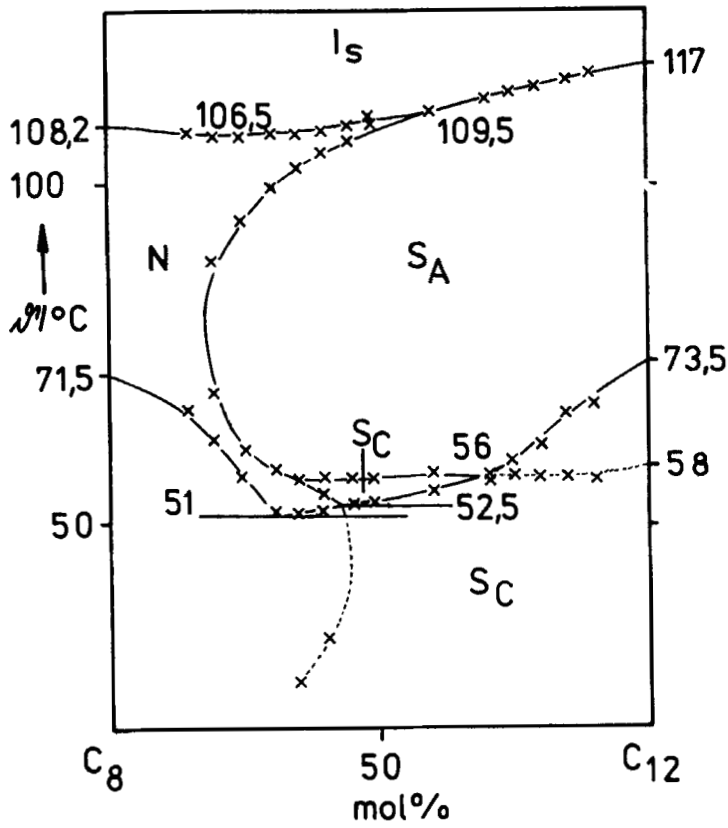

FIGURE 3

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