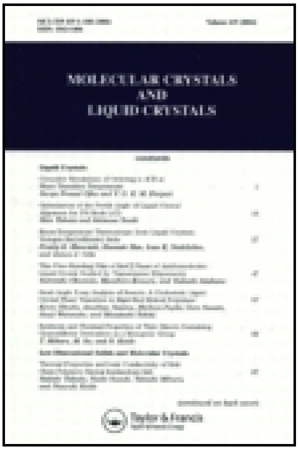

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Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds. III. Systems of Homologous n-Alkyloxyphenyl 4-[4-n-alkylcyclohexanoyloxy]-benzoates

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Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds III. Systems of Homologous *n*-Alkyloxyphenyl 4-[4-*n*-alkylcyclohexanoyloxy]-benzoates

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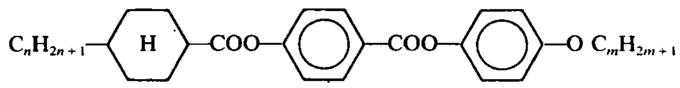
Reentrant nematic phases have been found in binary systems consisting of homologous terminal-non-polar compounds (*n*-alkyloxyphenyl 4-[4-*n*-alkylcyclohexanoyloxy]-benzoates). X-ray investigations showed that the S_A phases of both of the pure components and of binary mixtures are of the monolayer type. In some mixed systems the new phase sequence, N S_A N_{re} S_C S_B was observed.

Keywords: reentrant nematic phase, binary mixtures, terminal non-polar compounds

1. INTRODUCTION

In the majority of our binary reentrant systems, which are composed of terminal-nonpolar (t.n.p.) compounds, *n*-heptyloxyphenyl 4-[4-ethylcyclohexanoyloxy]-benzoate was used as the nematogenic component.[1,2,3] This substance exhibits a nematic phase over a wide temperature range and, in addition, forms a metastable S_C phase. In contrast, the long-chain homologues of this compound form S_A phases, mostly in the sequence N S_A S_B, but in some cases the sequence N S_A S_C S_B occurs. When the nematogenic compound and the polymorphic compound exhibiting an S_A phase (see Table I) are combined, the principal requirements for the production of a reentrant nematic phase appear to be satisfied.[2,3] All of the compounds we have used have closely related chemical structures. This may make it easier to discuss the factors influencing reentrance than is possible for systems involving terminal-polar (t.p.) species.[4]

TABLE I



n	*m*	K		S_B		S_C		S_A		N		Is
2	7	·	62	—		(·	41.5)	—		·	183	·
2	8	·	66	—		—		—		·	200	·
3	4	·	70	—		—		—		·	220	·
3	5	·	66	—		—		—		·	214.5	·
4	4	·	72	(·	57)	—		·	93	·	213	·
5	7	·	66	·	70	·	89	·	149	·	199	·
6	7	·	64	·	94	—		·	168	·	192	·
6	8	·	59	·	69	·	97	·	154	·	183	·
7	7	·	67	·	92	—		·	169	·	187	·

K: crystalline solid S_A, S_B, S_C: smectic A, B, C
N: nematic phase
Is: isotropic liquid
In some cases the transition temperatures differ slightly from those reported in Reference 5. In contrast to the observations described in Reference 5, for the homologues 5/7 and 6/8[a] in addition to the S_A and S_B phases an S_C phase was found.

[a]The members of the homologous series will be designated by the numbers *n* and *m*, respectively.

2. SUBSTANCES

Members of the homologous *n*-alkyloxyphenyl 4-[4-*n*-alkyl-cyclohexanoyloxy]-benzoates were synthesized by Deutscher *et al.*[5] The phase sequences and transition temperatures of the homologues studied are shown in Table I.

3. PHASE DIAGRAMS

The phase diagrams of the binary systems were studied with a polarizing microscope (Amplival, VEB Carl Zeiss Jena) using the contact method[6] and by determining transition temperatures of samples made up at specific concentrations. The layer spacings of the S_A phase were measured by X-ray diffraction using small angle equipment.

Binary systems composed of a component A having only monomorphism, N and a compound B having the polymorphism, N S_A S_B:

System 2/8–4/4 (Figure 1):

The mixed-phase S_A region is restricted to high concentrations of the B component, whereas the metastable S_B mixed phase region is observed over a wide concentration range. A N_{re} phase does not occur but the S_A–N curve falls steeply indicating a tendency towards reentrance and suggesting that it N_{re} phases may occur in related systems.

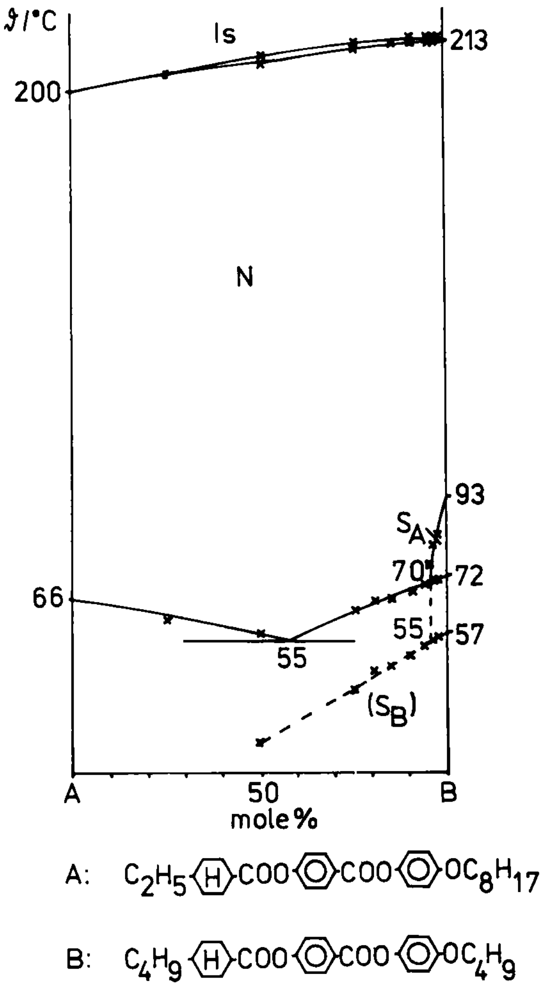


FIGURE 1

Systems 3/4–6/7; 3/5–6/7; 2/8–6/7 and 2/8–7/7 (Figures 2, 3, 4 and 5):

In all of these phase diagrams the same topological situation occurs. In the mixture shown in Figure 2 the slope of the S_A—N curve does not change sign but in the other systems the S_A—N curve falls vertically and then bends toward the B component creating an area of reentrant nematic phase. In all of these systems, an intermediate S_C phase occurs which terminates the N and N_{rc} phases at lower temperatures.

Binary systems composed of compounds A and B where either one or both have an additional S_C phase

System 2/7–6/7: Polymorphism $N(S_C)$–N S_A S_B (Figure 6):

The phase diagrams have the same general topology as Figures 2–5 but the stable S_C phase now extends from the metastable S_C phase region of the compound A.

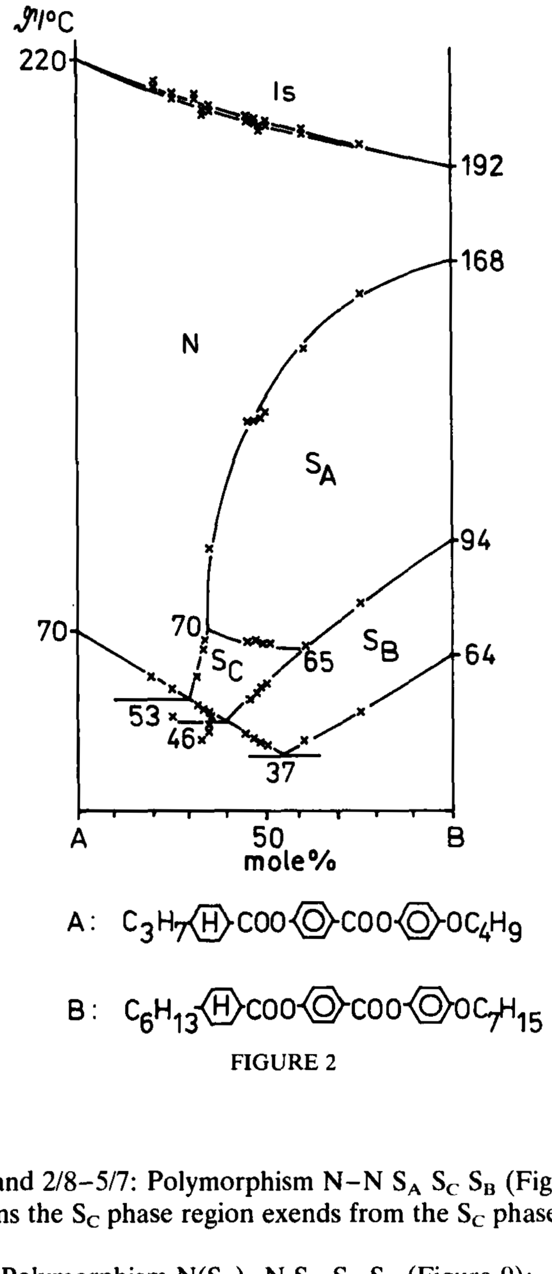


FIGURE 2

System 3/5–6/8 and 2/8–5/7: Polymorphism N–N S_A S_C S_B (Figures 7, 8):

In these systems the S_C phase region exends from the S_C phase of compound B.

System 2/7–6/8: Polymorphism N(S_C)–N S_A S_C S_B (Figure 9):

The stable and metastable region of the S_C phase are parts of a band of complete miscibility which links the S_C phases of the pure components. X-ray investigations showed that the S_A phase of the pure smectogenic compound 6/8 and of the mixed phase region are both of the monolayer type. For example, for a mixture 70 mole-% of compound 6/8, a layer spacing d of 33.5 Å was found. For comparison, the

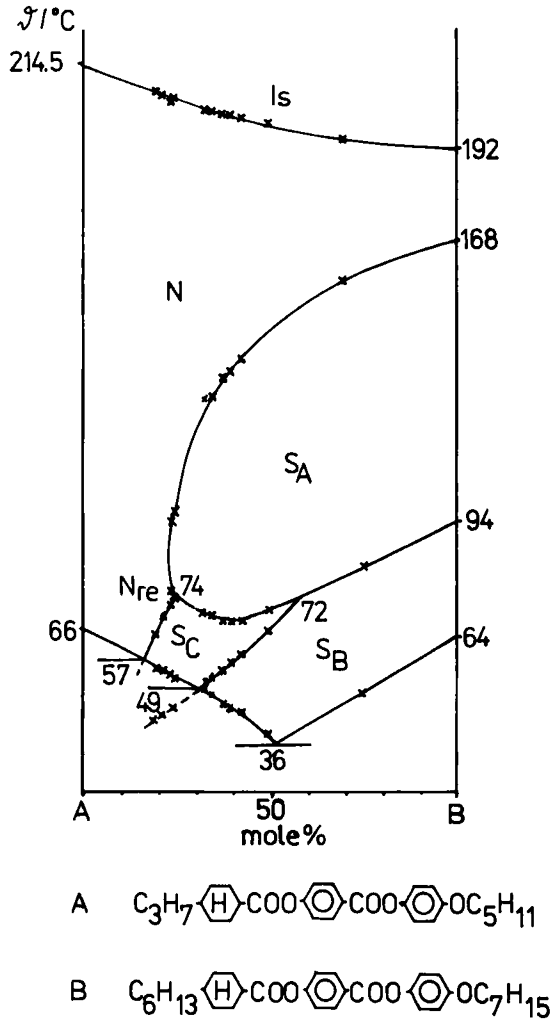


FIGURE 3

average molecular length calculated as $\mathrm{I} = x_A L_A + x_B L_B$[7] is 36.1 Å ($x_A$, x_B-molar fractions of the compounds A and B, L_A, L_B-molecule lengths of the compounds A and B)

4. DISCUSSION

Reentrant nematic phases were found in binary systems composed of homologous compounds. The central aromatic part of all molecules was the same (Table I) and only the terminal alkyl chains were varied. As can be seen from Table I, those

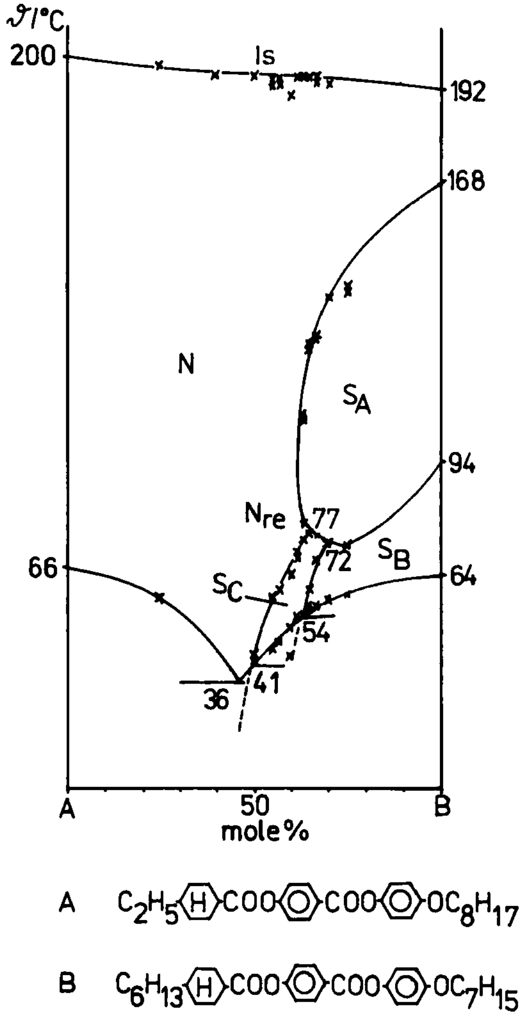


FIGURE 4

homologues with at least one short side chain (n = 2, 3) have a nematic phase with a wide temperature range. In addition to nematic phases, those homologues with longer side chains form an S_A phase and other smectic phases (S_B, S_C).

The combination of the nematogenic compounds and the longer chain polymorphic compounds, leads to phase diagrams of the type shown in Figure 10. With the exception of the system 2/8–4/4 (Figure 1), a broad field of mixed S_A phase was always found. The S_A–N transition temperatures fall increasing steeply with increasing concentration of the nematogenic compound A. With the exception of

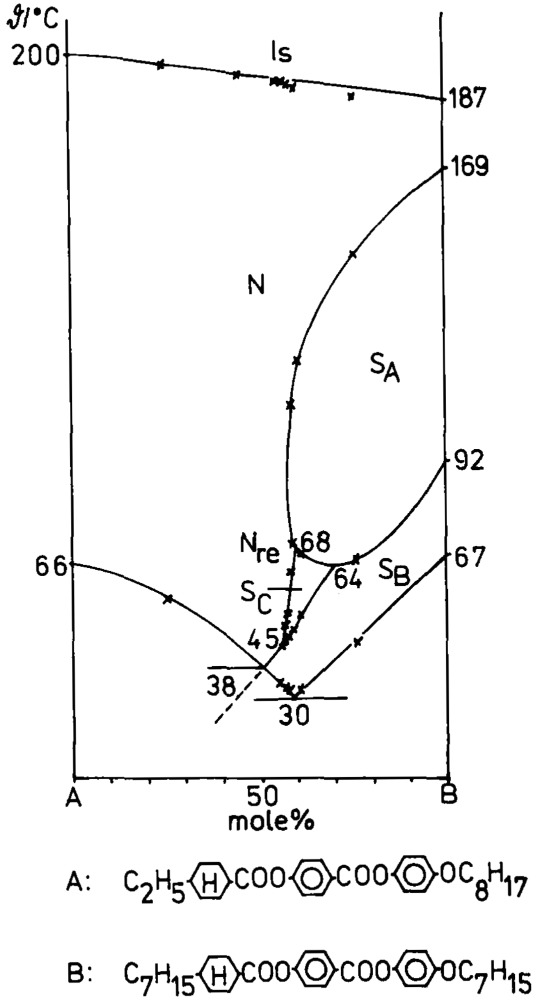


FIGURE 5

system 3/4–6/7 (Figure 2), a maximum concentration is observed and the S_A–N transition curve changes in sign. In all cases, the range of the N_{re} phase is small and is closed with a S_C phase at lower temperatures (Figure 10). In the systems shown in Figures 2, 3, 4 and 5 these S_C phases are intermediate phases. In the systems shown in Figures 6, 7 and 8 they extend from the S_C phase of one of the components.

In Figure 9 where both components have a S_C phase, complete miscibility was found. It is interesting that the occurrence of the nematic reentrance does not appear to be correlated with the size of the S_A phase region (c.f. Figures 2 and 8).

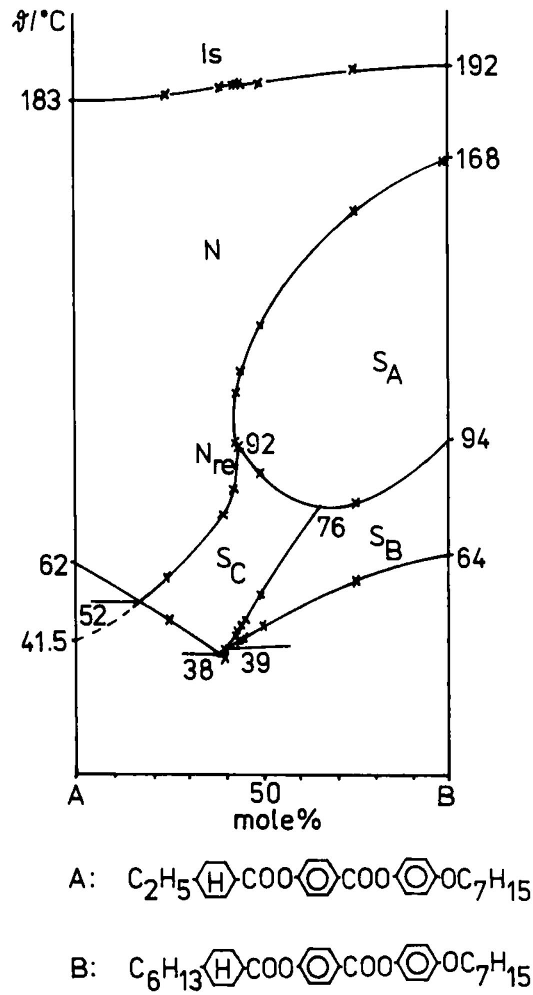


FIGURE 6

In a binary system with the short chain compound 4/4 no tendency towards the topological situation of Figure 10 was found (Figure 1). In system 3/4–6/7 shown in Figure 2, a borderline case of Figure 10 without a reentrant phase was achieved. The combinations 3/5–6/7, 2/7–6/7 and 2/8–6/7 (Figures 3, 6, 4) illustrate the way in which reentrance is very sensitive to the molecular structure.

In order to produce reentrant systems, no dramatic change in the chemical constitution of the phase systems is required. We have no details of the molecular order of the S_A phase in these systems. In the system 2/7–6/8 (Figure 9) a monolayer spacing of the pure smectogenic compound and of its mixed phases was found (see

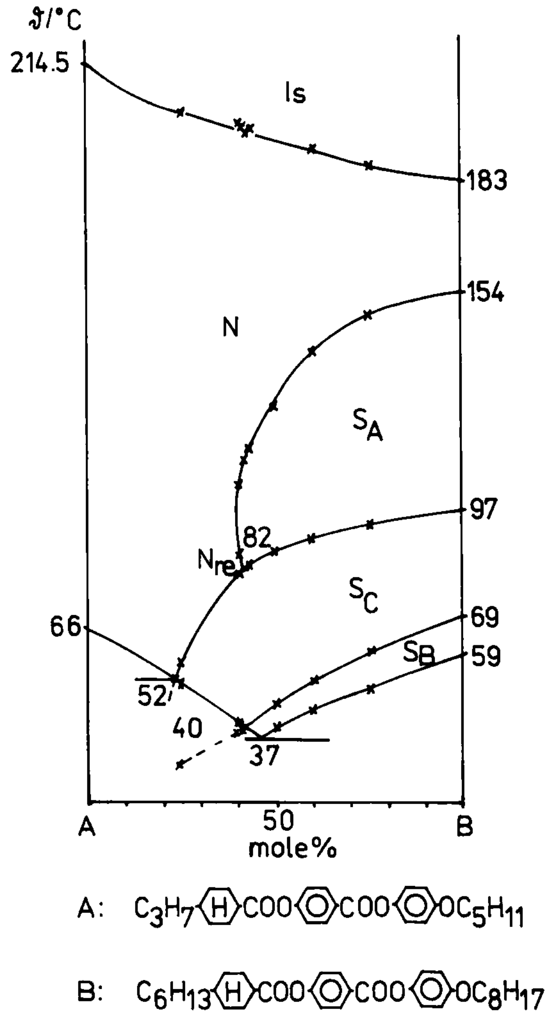


FIGURE 7

also Reference 1). But there are also examples of reentrant systems of t.n.p. compounds in which the layer spacing d is somewhat greater than the molecular length L ($^d/L \sim 1.05$).[8] Up to now, we have no quantitative information to help us to evaluate the causes of the reentrance effect in these systems. But we note the beginning of a theoretical treatment of t.n.p. systems in the work of Dowell.[9]

In several binary systems the new phase sequence, N S_A N_{re} S_C S_B was found. A similar phase sequence was observed in a system of t.p. compounds, although in that case, the S_C phase was a S_C antiphase and the S_A phase was of the S_{Ad}

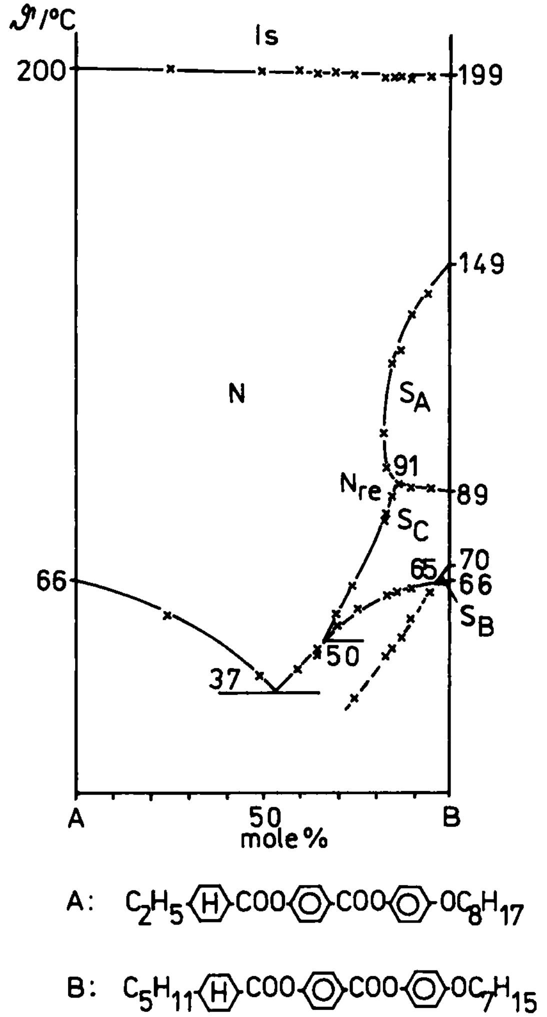


FIGURE 8

type.[10] Furthermore, in systems of the type shown in Figure 10 and described above (see also References 1, 2, and 3) a variant of a multicritical point occurs, which was first observed in binary systems of t.p. compounds.[11,12,13] When the S_C–N transition curve (Figure 10) intersects the S_A–N curve at higher temperatures than those of the maximum S_A concentrations, a well-known NAC point appears. In our reentrant systems, there is an N_{re} AC point, which may be a new type of a multicritical point. The situation occurring in the system 3/4–6/7 (shown in Figure 2) represents the transition from one type of behaviour to the other.

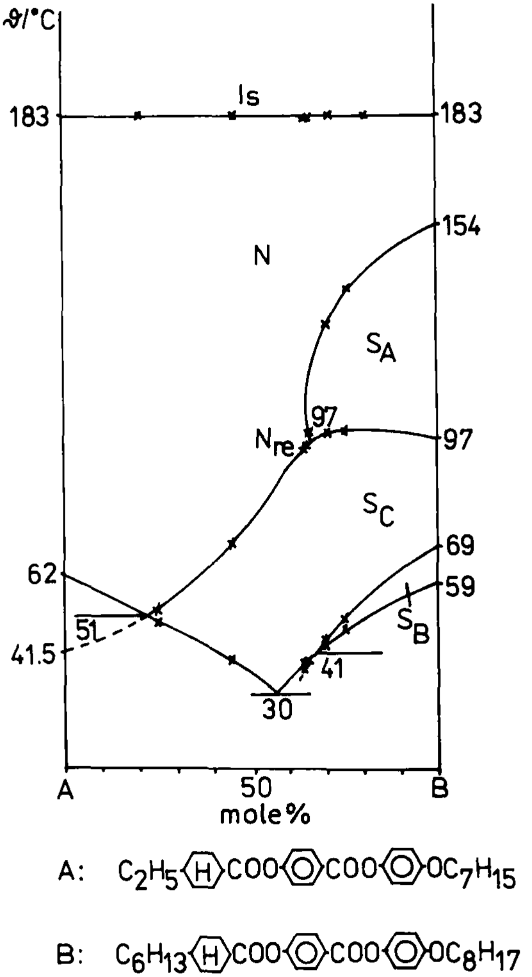


FIGURE 9

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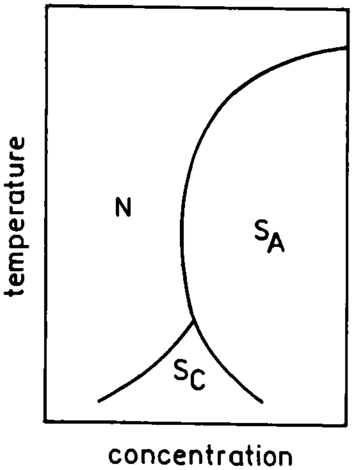

FIGURE 10 General shape of the transition curves S_A–N, S_C–N, and S_A–S_C.

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