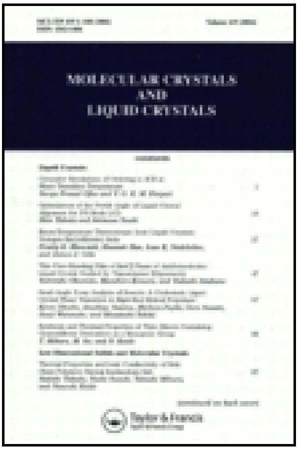

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Liquid Crystalline Phases in the Homologous Series of Terephthalylidene-BIS-[4-n-Alkylanilines]

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Version of record first published: 20 Apr 2011.

To cite this article: L. Richter , D. Demus & H. Sackmann (1981): Liquid Crystalline Phases in the Homologous Series of Terephthalylidene-BIS-[4-n-Alkylanilines], Molecular Crystals and Liquid Crystals, 71:3-4, 269-291

To link to this article: http://dx.doi.org/10.1080/00268948108072327

Mol. Cryst. Liq. Cryst., 1981, Vol. 71, pp. 269–291
0026-8941/81/7104-0269/$06.50/0

Printed in the United States of America

Liquid Crystalline Phases in the Homologous Series of Terephthalylidene-BIS-[4-*n*-Alkylanilines]†

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(*Received August 15, 1980*)

The liquid crystalline polymorphism in the homologous series of terephthalylidene-bis-4-*n*-alkylanilines was investigated by miscibility experiments. The variants of polymorphism found in the members with carbon atoms $n = 3$ to $n = 10$ in the alkyl chains can be derived from a variant H G F I C A N through the absence of one or several phases. Besides the known phases H, G, F, C, A, and N, the new phase type I was found. The results are discussed in connection with investigations on structure.

1 INTRODUCTION

In the congress reports of the Halle Liquid Crystal Group,[1-3] results of studies of the determination of the phase types and their relations in the homologous series of 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkoxyphenyl]pyrimidines (AAOP), the terephthalylidene-bis-[4-*n*-alkylanilines] (TBAA), and the *N*-[4-*n*-alkoxybenzylidene]-4-*n*-alkylanilines were published in summary form.

After the presentation of detailed results for the series AAOP,[4] the investigation of the TBAA series is described now. According to initial investigations by Doucet *et al.*[5] on the phase structures for the fourth member (TBBA) of this series, substances with a high degree of liquid crystalline (l.c.) polymorphism could be expected. This was confirmed in the first comprehensive report on their synthesis by Neubert and Maurer.[6]

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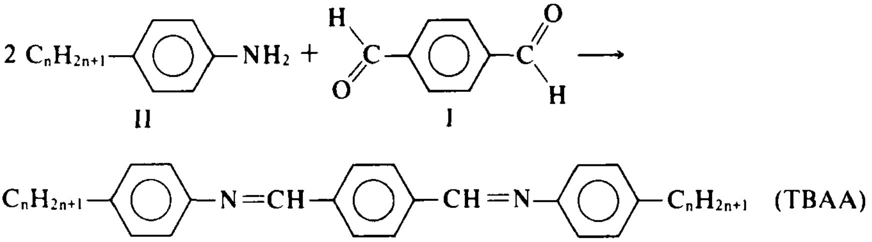
† Paper no. 25: Relations of Isomorphism in Liquid Crystalline Phases.

We intend to include these phases in the system of polymorphism of l.c. phases through the criterion of miscibility. At the same time a characterization of these phases and the phase transitions by X-ray measurements and calorimetric investigations has been given.[7,8]

2 MISCIBILITY IN THE HOMOLOGOUS SERIES OF TBAA

2.1 Substances and Method

The synthesis was done by condensation of terephthalaldehyde (I) with the corresponding 4-*n*-alkylaniline (II):



By repeated crystallization, purification was accomplished; the transition temperatures for the single members $n = 3$ to $n = 10$ are plotted in Figure 1.

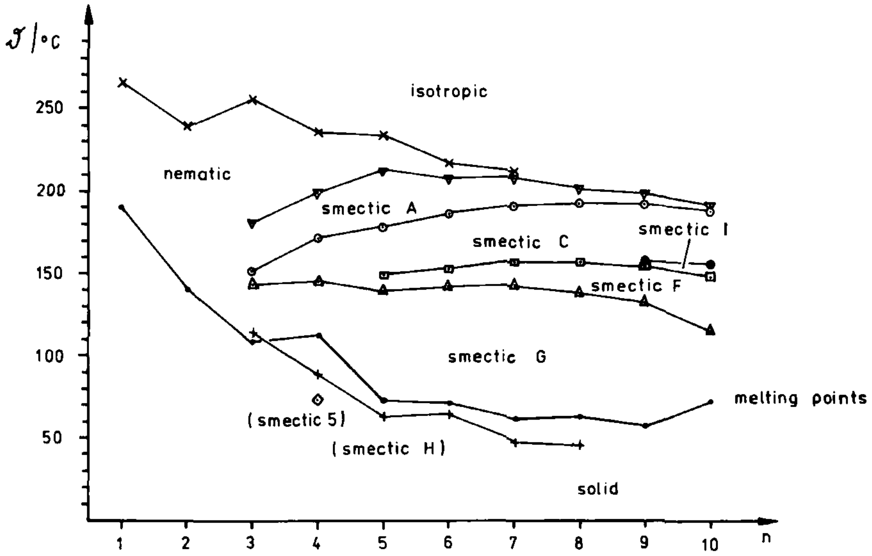


FIGURE 1 Phase transition temperatures for the TBAA series.

They were confirmed by miscroscopy and by calorimetric (Perkin Elmer DSC 2) measurements. The numerical data were listed by Wiegeleben *et al.*[8]

The following abbreviations are used for the alkyl groups Pr = propyl, B = butyl, P = pentyl, Hp = heptyl etc. They may then be used to represent the substances (e.g.: $n = 7$, TBHpA).

The phase diagrams of the various binary systems were investigated by heated-stage microscopy. The crosses in the diagrams denote the observed beginning or ending of a phase transition. If sharp transitions were not observable, these are indicated by lines (bars).

Certain transitions could be observed only in the super-cooled (metastable) region. The corresponding transition curves are drawn with dashed lines.

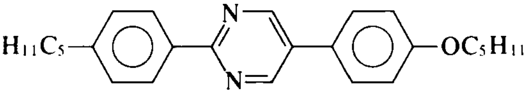
2.2 Miscibility between the members of the TBAA series (see Figures 2-7)

System II was first investigated by Sakagami *et al.*[9] and later by Goodby *et al.*[10] Concerning the miscibility relations of the phases, named here G F C A N, the results of the three investigations agree. (Because of the altered code, smectic G is used here instead of smectic H in Ref. 10 see 3.1). The diagram in Figure 3 determines more exactly the trend of the transition curves with concentration and gives additionally the curve G-H in the metastable region.

The first investigations[9] led to another code sequence of the phases of TBPA (B III C A N) because of the classification of the third smectic phase of TBBA as a B phase at that time (see system X).

2.3 Miscibility between members of the TBAA series and reference substances (see Figures 8-12)

2.3.1 Reference substances 1) 2-[4-*n*-pentylphenyl]-4-[4-*n*-pentyloxyphenyl]pyrimidine (PPOP)



Cr 79.5 (H 61.5) G 102.4 F 113.1 C 144.8 A 210 Is

In this substance the F and G phases were first found in 1971;[11] with respect to the H phase see Refs. 1, 2, 4 and the comments in Section 4.1.

2) 2-[4-*n*-butylphenyl]-5-[4-*n*-butyloxyphenyl]pyrimidine (BBOP)

Cr 90.3 (H 73) G 113.7 C 120.7 A 214 Is

Classification see Refs. 1, 2, 4, 15.

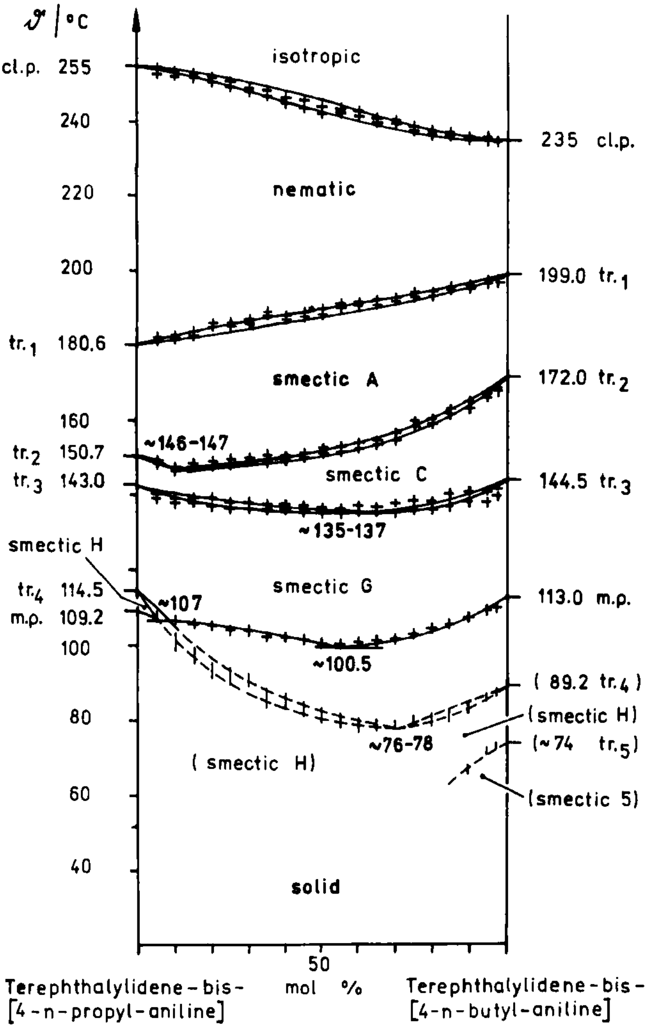
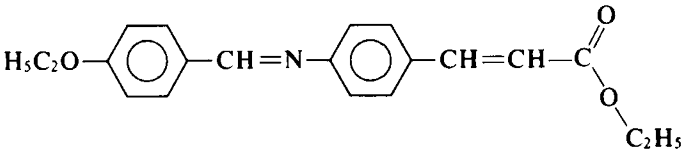


FIGURE 2 System I (TBPrA—TBBA)

3) Ethyl 4-[4-ethoxybenzylideneamino]cinnamate (EEBC)



Cr 80.3 B 119.7 A 158.3 N 164.9 Is

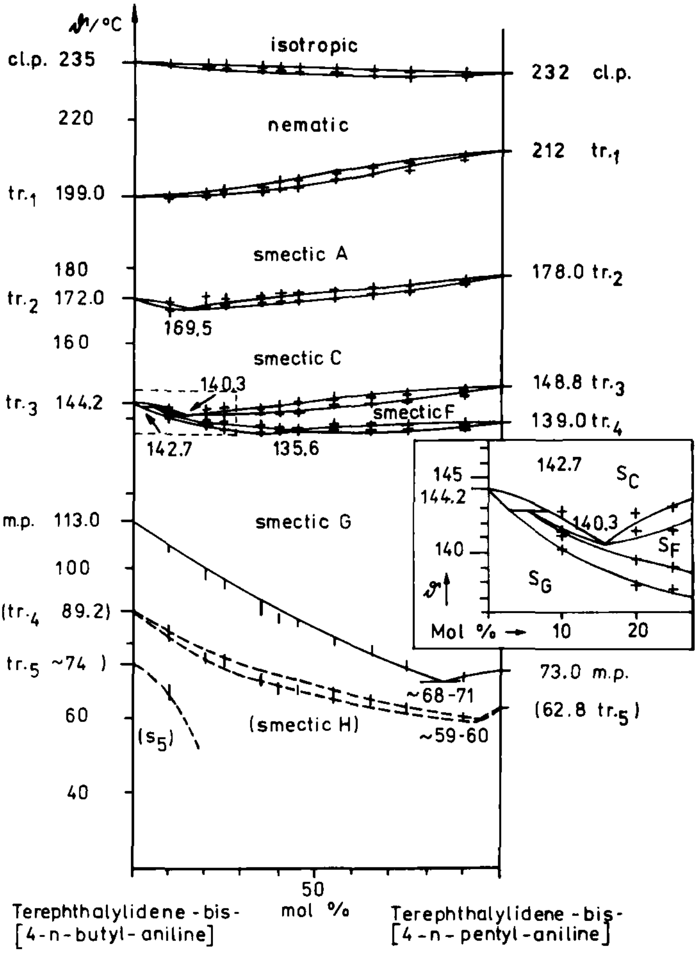


FIGURE 3 System II (TBBA—TBPA)

This is the standard substance for classification of B phases. Classification in 1959, Ref. 12; see also Ref. 13.

4) *n*-propyl 4-[4-*n*-octyloxybenzylideneamino]cinnamate (PrOBC)

Cr 66.1 B 106.3 A 151.1 Is

Classification in Ref. 14.

2.3.2 Phase Diagrams The new investigation of system IX (Figure 10) corrects results which were published in Ref. 15, Figure 4. A great number of preparations with different single concentrations now allows us to recognize

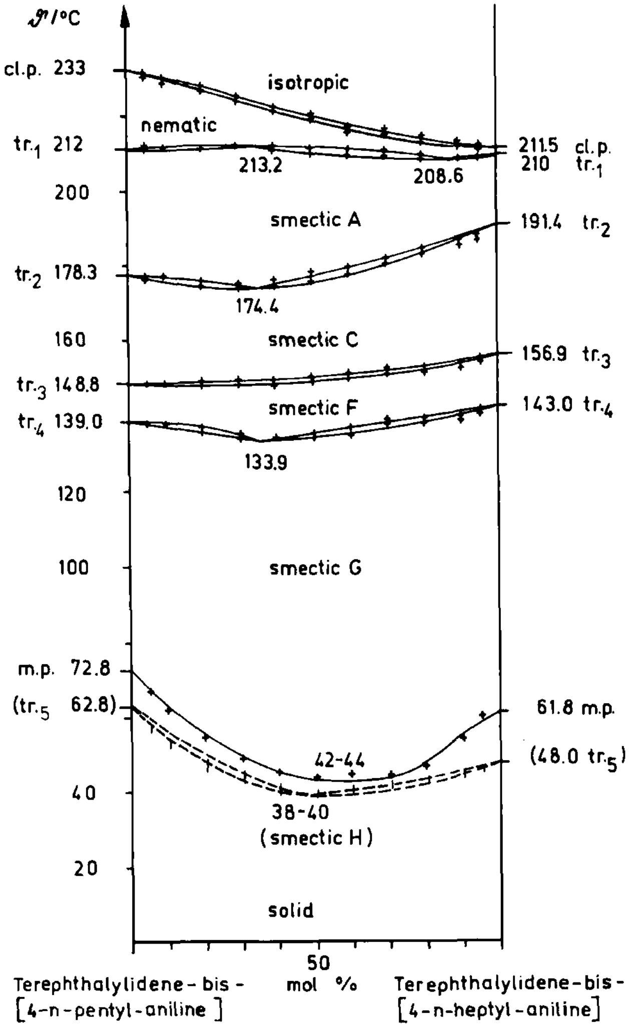


FIGURE 4 System III (TBPA—TBHpA)

exactly the transition curves relating to the C, F, and G phases. The only preparation investigated at lower temperature and 20 mol% in the older measurements led to an incorrect extrapolation of a transition curve.

Further on, the transition curve G-H in the metastable region can now be fixed.

The broad ranges of mixed F phases relate to a region of stabilized, mixed phase originating from unstable or latent F phases of the two compounds. This is suggested by the position of the two compounds in their homologous

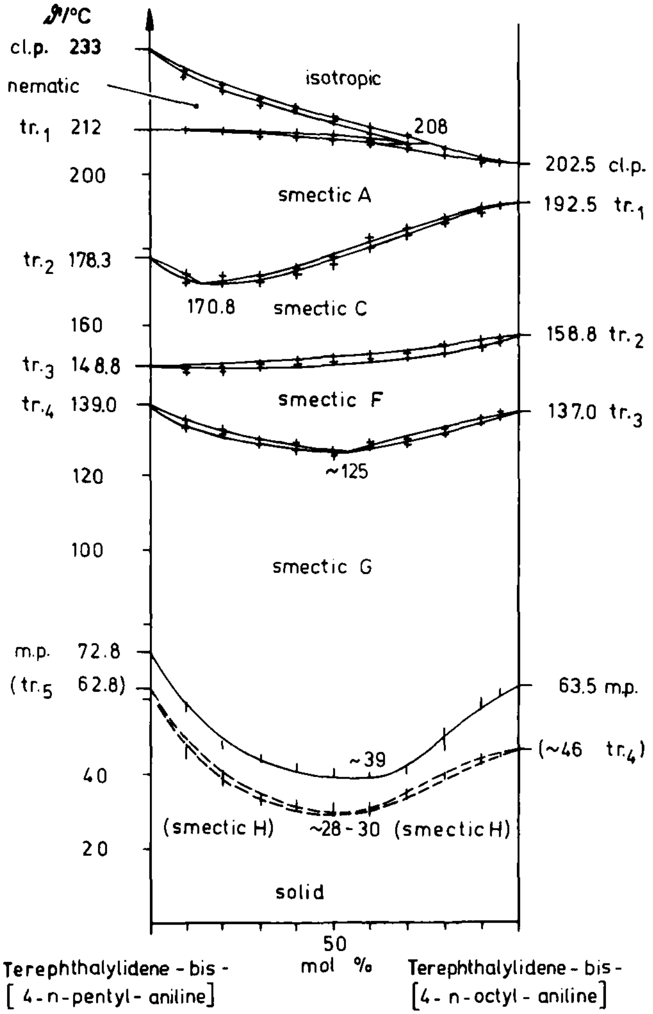


FIGURE 5 System IV (TBPA—TBOA)

series and the trends of the transition temperatures for the phases in these series (see Figure 1).

A renewed investigation of system X gave the results shown in Figure 11. They show a most important difference from the previous investigation (Figure 3 in Ref. 15). There is an interrupted miscibility between the phases designated now as B and G phases. The region between the two mixed phases B and G is small and possesses a slight dependence on temperature. The choice of small changes in concentration of the probes allowed the discovery of this two phase region and the existence of the intermediate F phase region. Therefore,

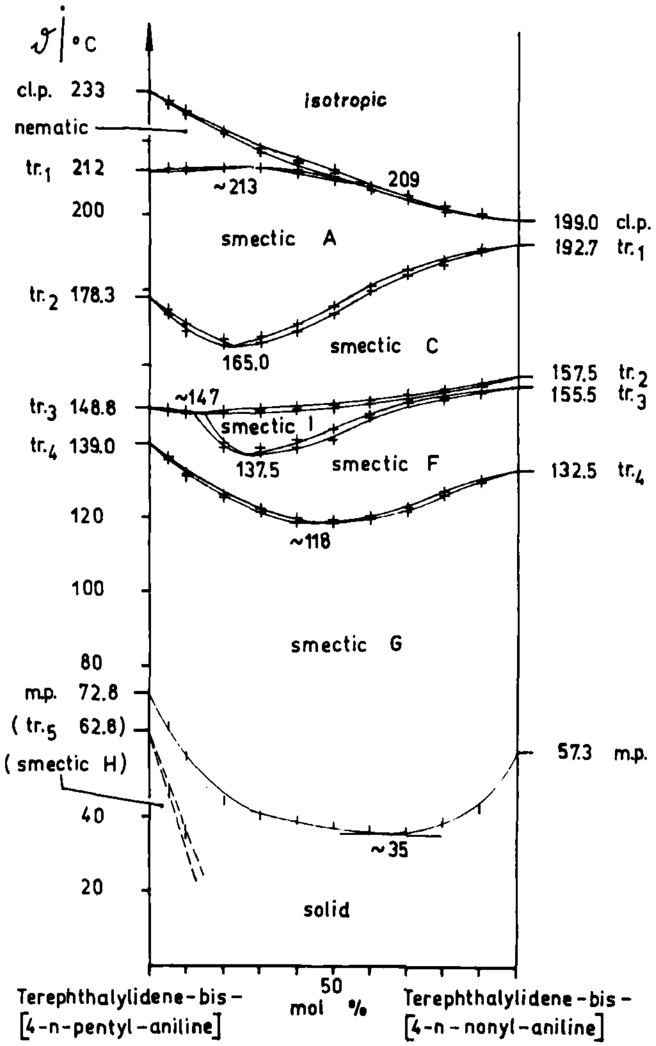


FIGURE 6 System V (TBPA—TBNA)

contrary to previous results, no complete miscibility between the phases B and G exists, and the necessity for the old designation of the G phase of TBBA as a B phase disappears.

System XI is analogous to system X. The gap in miscibility between the B and G phases is broader and shows a strong dependence on concentration. An extrapolation to the pure PrOBC compound is possible, and shows a transition B-G. Because of spontaneous crystallization, this transition in the metastable region of the pure compound could not however be observed directly.

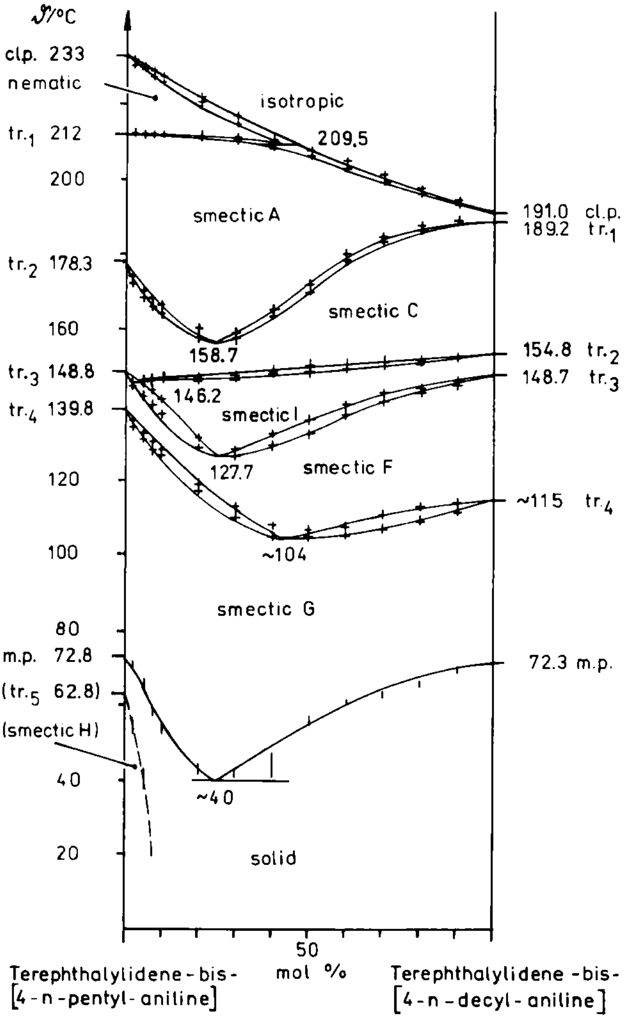


FIGURE 7 System VI (TBPA—TBDA)

3 REMARKS ON TEXTURES

The observation of some phase transitions by texture changes was demonstrated in Refs. 4, 6, 20. Phase transitions involving I phases, especially in the case of the transitions C-I, I-F and I-G are not however strongly distinguished by texture changes. Separate preparations with paramorphotic fan-shaped or schlieren textures of the F and I phases did not exhibit *characteristic* distinguishing features although we can certainly follow the sequences of textures

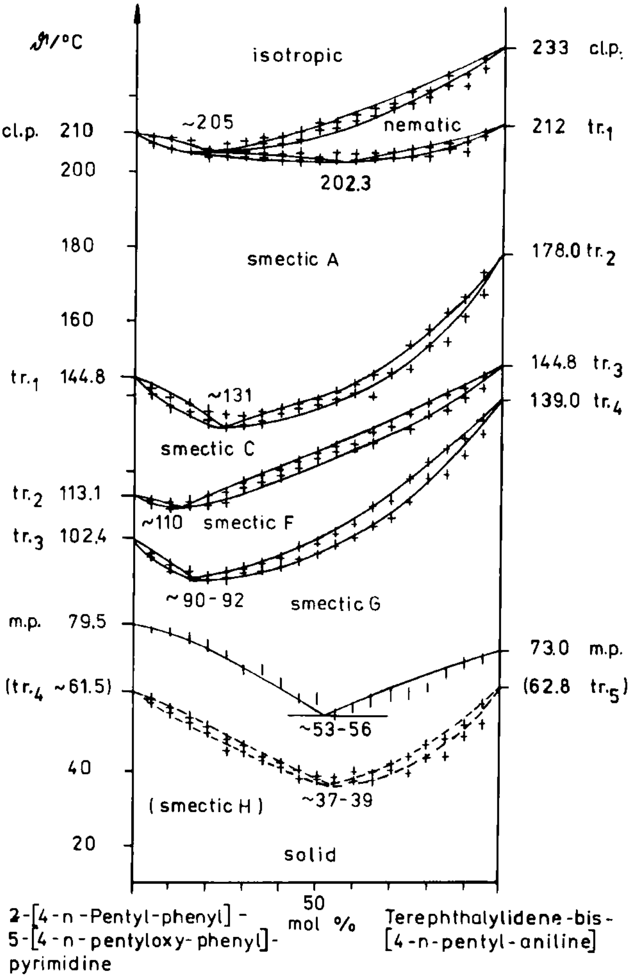


FIGURE 8 System VII (PPOP–TBPA)

with decreasing temperature, starting from the well-known schlieren textures of smectic C. The recognition of the textures of smectic I and F is favored with schlieren textures (Figures 13 and 15). The transition I-F (Figure 14) was marked by characteristic transition mosaics which coalesced to mosaic-like variants of the schlieren textures of smectic F (Figure 15). In these variants, only a few remnants of broad schlieren brushes and sharp inversion lines occurred.

Very slight changes were also observable at the transitions G-H and H-5 (TBBA). A comparison of partial sequences involving paramorphotic fan-

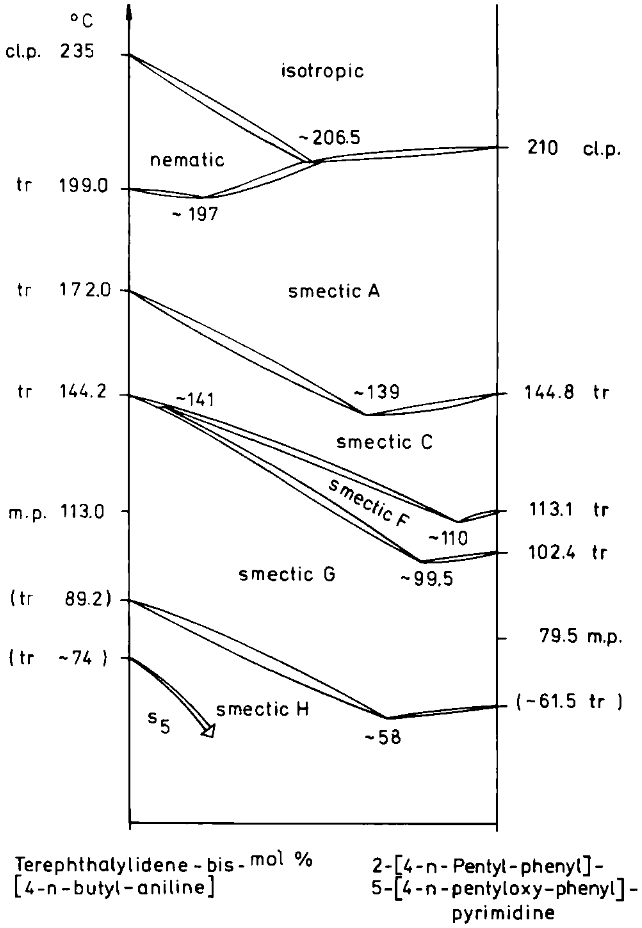


FIGURE 9 System VIII (TBBA—PPOP). Results from a contact preparation.

shaped textures and mosaic textures of phases G and H (TBPA) revealed slight distinctions (Figures 16, 18–20). For the paramorphotic fan-shaped textures, the transition G-H showed a transient cross-hatching of homogeneous domains (Figure 17, see examples indicated by arrows). These observations agree with those of Goodby *et al.*[20] The stable texture of the unclassified phase (smectic 5) of TBBA showed very similar features to those of smectic H. Starting from the mosaic texture of smectic H, with decreasing temperature during the first cycle, the mosaic borders became broader during the transition and resembled additional mosaics in smectic 5.

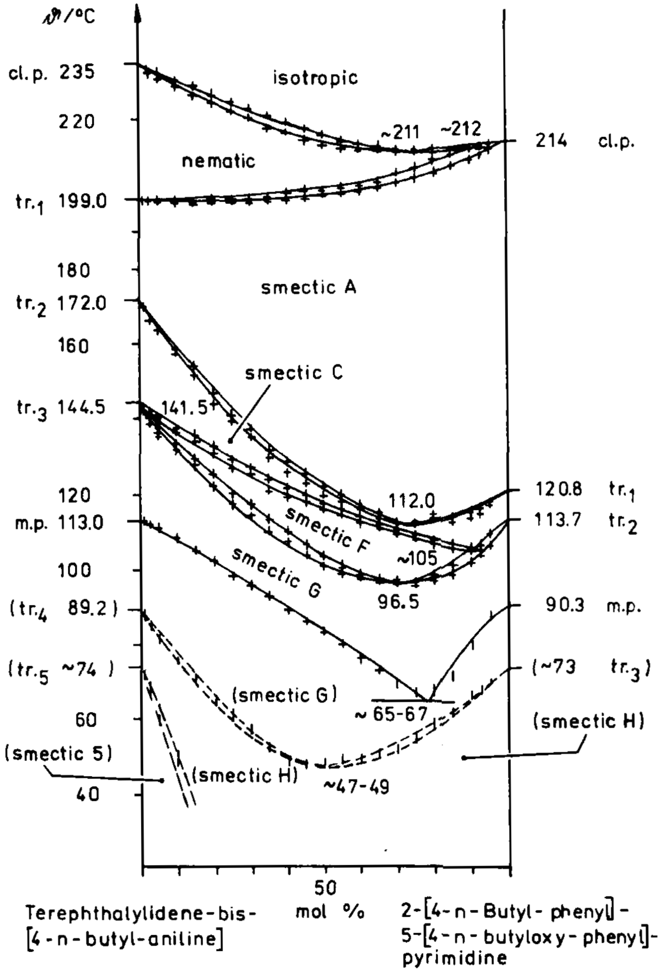


FIGURE 10 System IX (TBBA—BBOP)

In all cases, especially in samples not carefully prepared and selected, confusion was possible because of slight texture changes occurring in homogeneous regions of phase and often indicating transition changes with temperature. A strong indication of real phase transitions is given by a regular dependence of these changes on concentration in binary systems, giving a transition line, which follows a thermodynamic principle. In cases of doubt, confirmation by other methods is valuable.

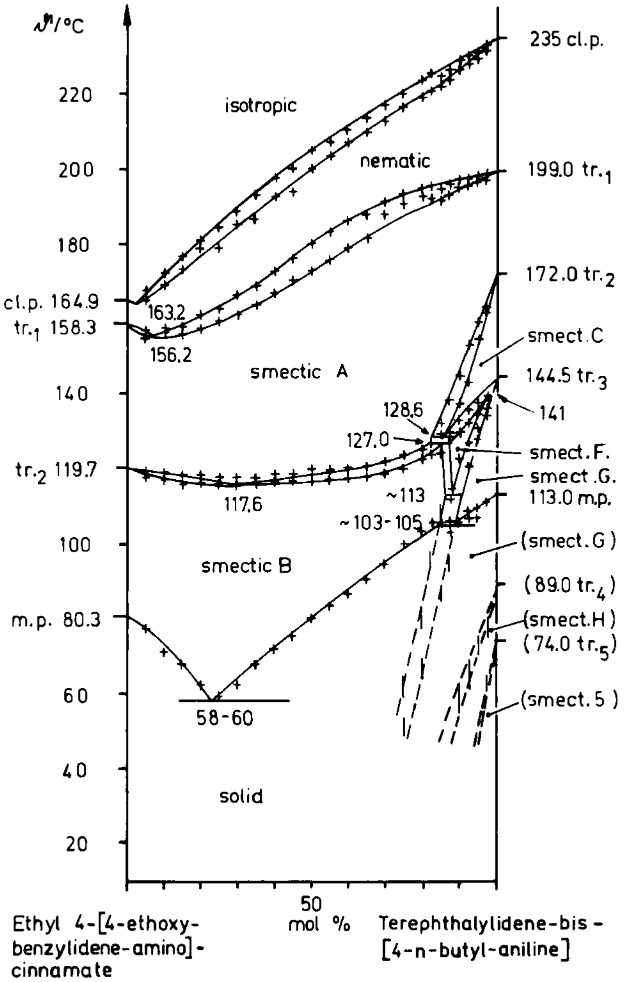


FIGURE 11 System X (EEBC—TBBA)

4 DISCUSSION

4.1 Summary of the investigations on miscibility: Classification of the phases: New phase type I

In Figure 21, the results of the investigations of miscibility are summarized. The lines connect any two substances the miscibility of which has been investi-

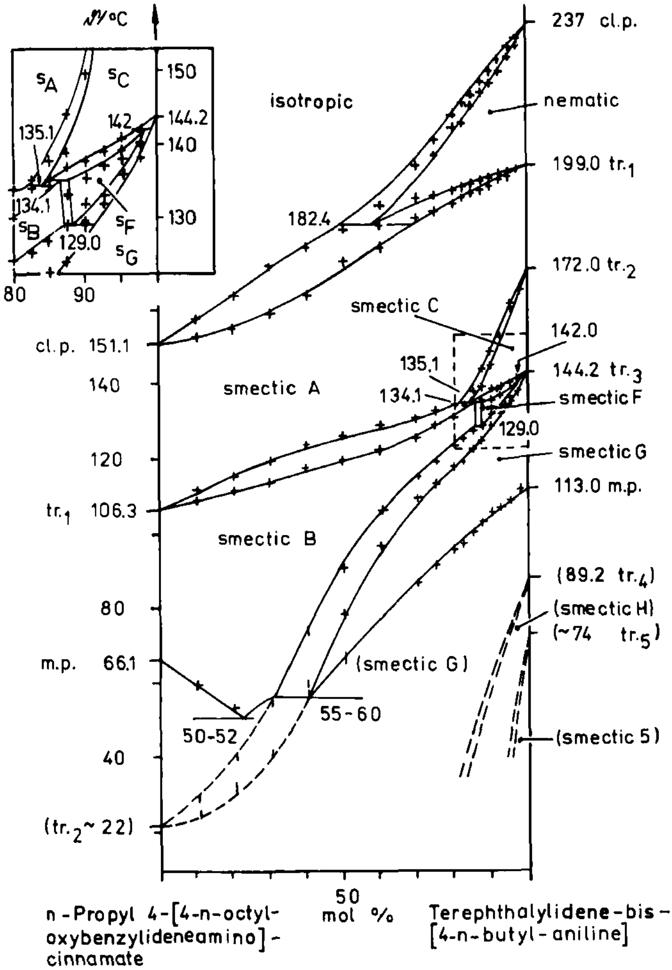


FIGURE 12 System XI (PrOBC—TBBA)

gated in a binary system. The numbers refer to the numbers used for the systems in sections 2.2 and 2.3.2. At the same time, these lines characterize complete miscibility between the phases of the same type which are designated by the same letter. The variants of polymorphism of each substance are listed below the symbols for the substances. In the systems presented, complete miscibility between phases of the same type has always been found.

Besides the phases of the types N, A, and C in the TBAA series, there exist the liquid crystalline phases I, F, G, and H. According to the principle of denomination of l.c. phases by miscibility,[16] the designation F and G is derived

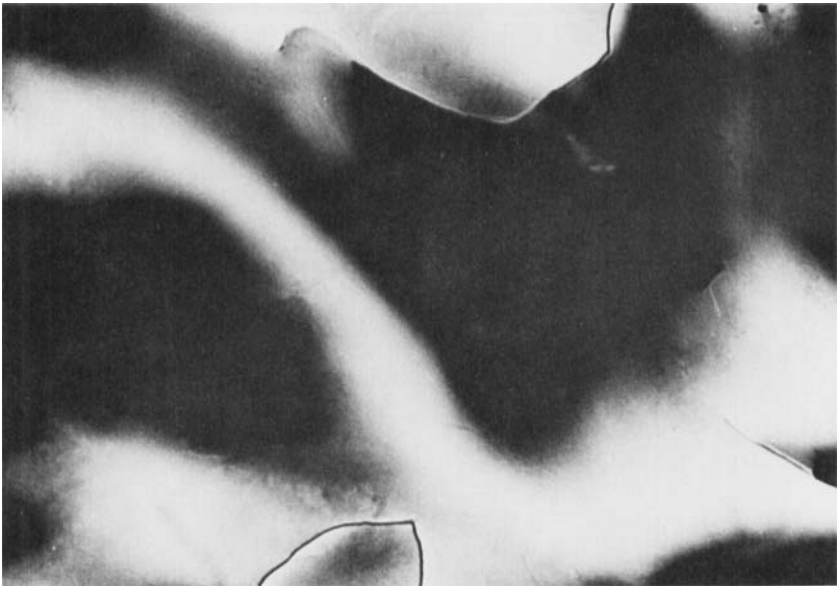


FIGURE 13 TBNA, smectic I; schlieren texture with sharp inversion lines resembling a partly mosaic-like appearance; 157°C, × 150.

FIGURE 14 TBNA, smectic I-F; transition mosaics; 155°C, × 150.

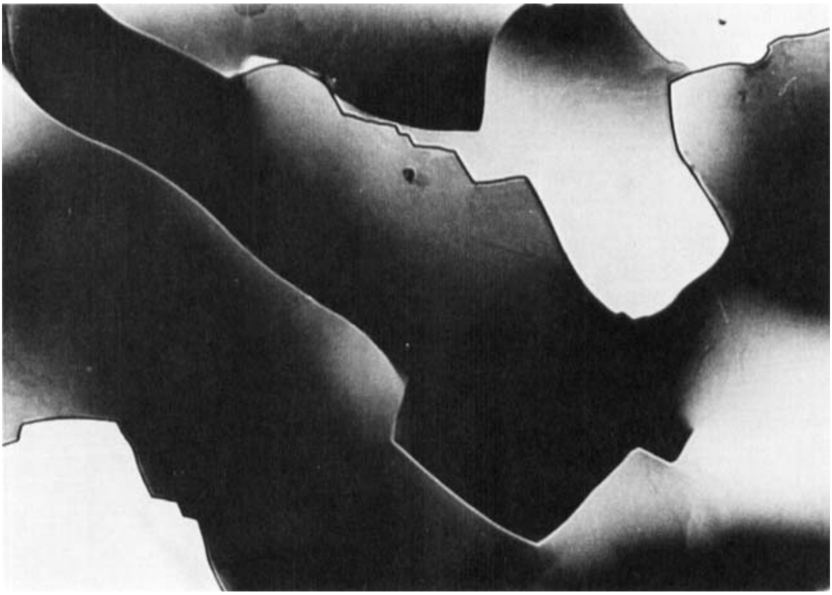


FIGURE 15 TBNA, smectic F; schlieren texture with sharp inversion lines; 143°C, × 150.

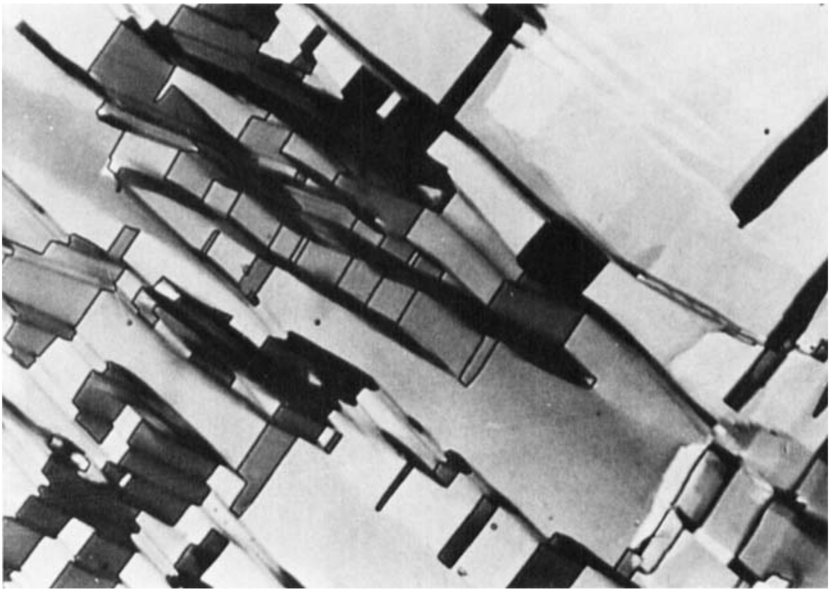


FIGURE 16 TBPA, smectic G; mosaic texture with paramorphotic boundaries; 70°C, × 150.

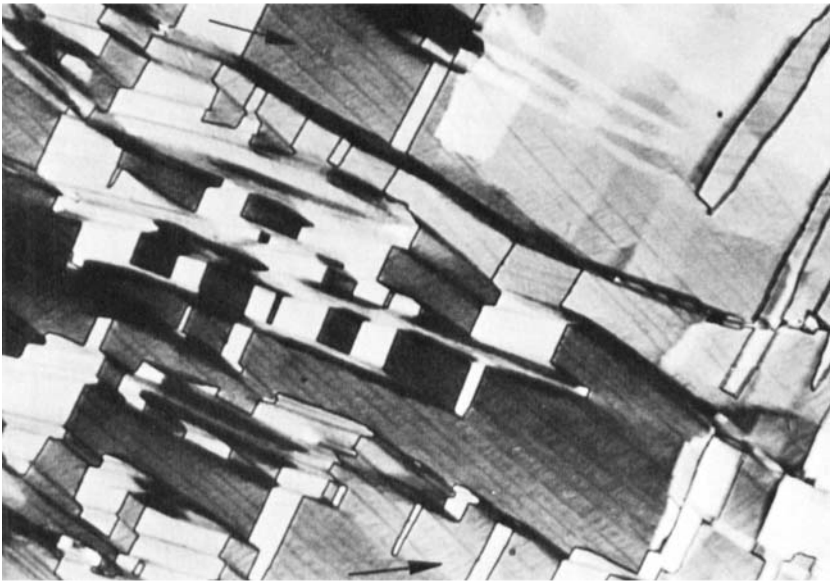


FIGURE 17 TBPA, smectic G-H; occurrence of a transient parquet-like pattern; 62.5°C, × 150.

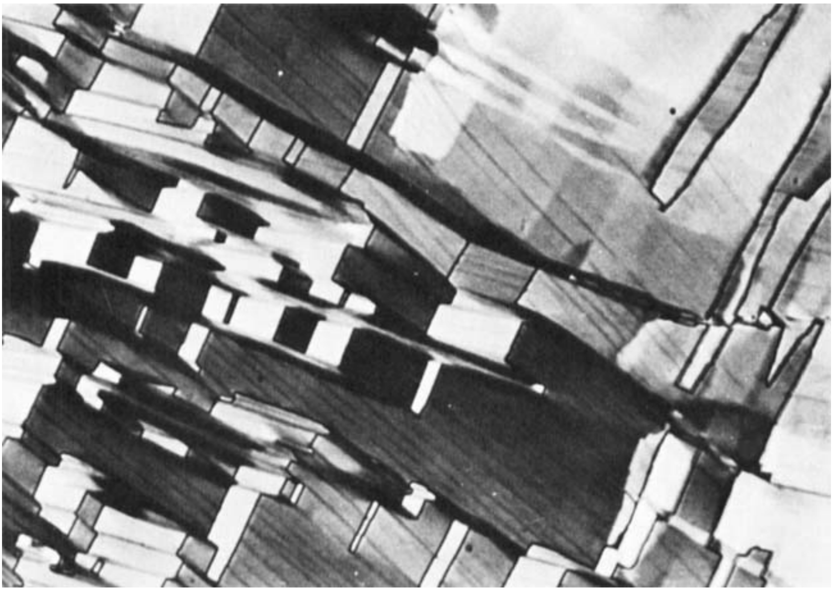


FIGURE 18 TBPA, smectic H; paramorphotic mosaic texture with a dislocated striation; 47°C, × 150.

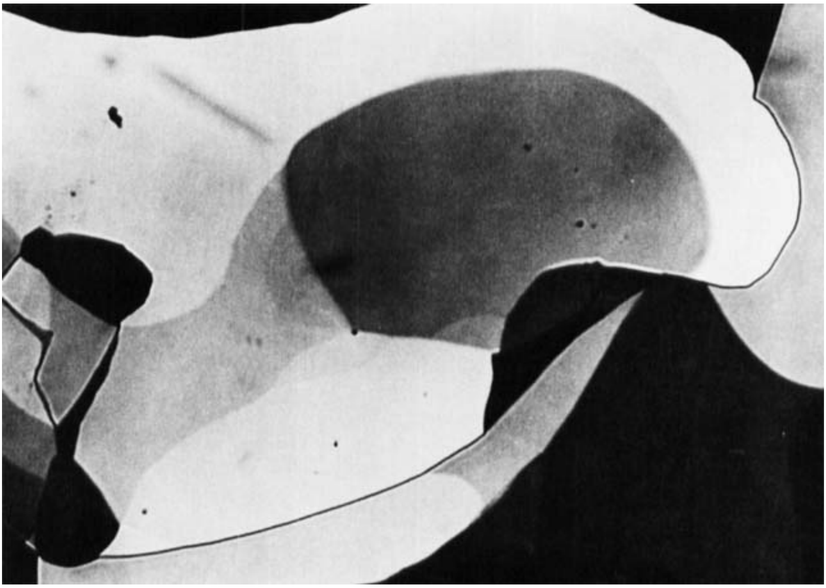


FIGURE 19 TBPA, smectic G; mosaic texture; 125°C, × 150.

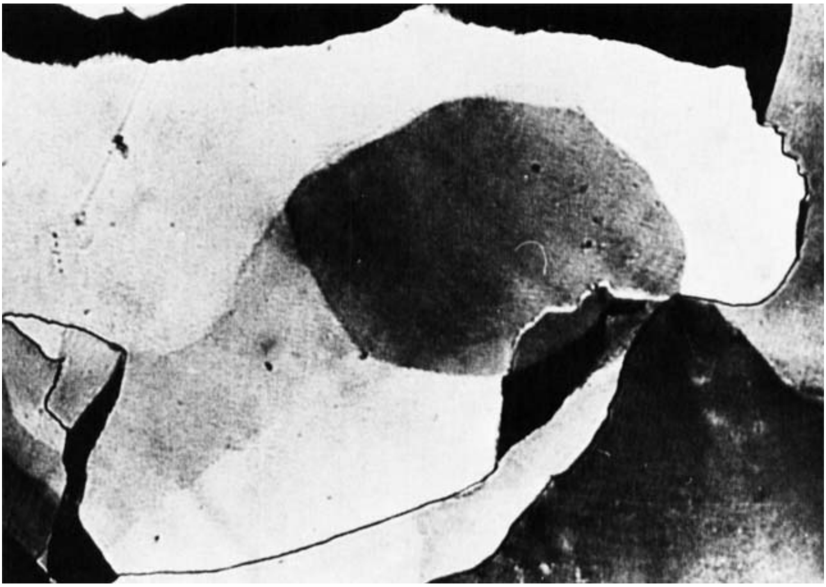


FIGURE 20 TBPA, smectic H; mosaic texture with granular pattern; 60°C, × 150.

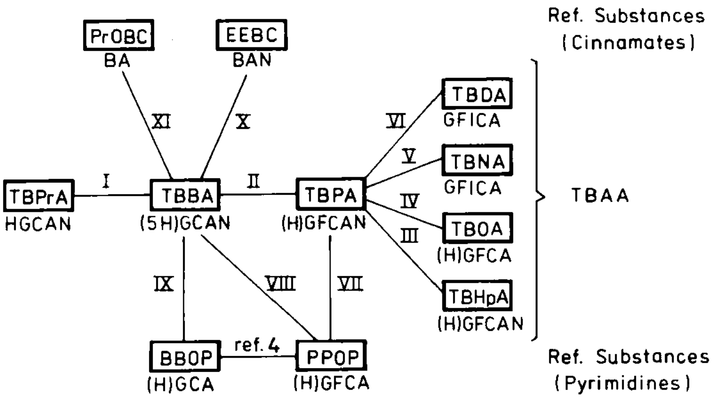


FIGURE 21 Schematic presentation of the miscibility relations for the TBAA series (Systems I XI).

from the F and G phases of the standard substance PPOP, in which the first F and G phases were found in 1971.[11] According to Ref. 4, the homologue BBOP can also be used as a reference substance for G phases. From the cycles relating to the binary systems II, VII, VIII, and IX, the appearance of phases F and G in TBPA and of phase G in TBBA was proved by the uninterrupted miscibility. From the phases F and G of these substances, the designation F and G was transmitted to the other corresponding phases F and G of the TBAA series in the systems I, III, IV, V, and VI.

In the compounds TBPrA, TBBA, TBPA, TBHxA, TBHpA, and TBOA of the TBAA series, as well as in the compounds BBOP and PPOP, phases have been found which appear at temperatures below the region of existence of the G phases. As can be seen in systems I, II, III, IV, VII, VIII, and IX, these phases are connected by regions of complete miscibility. Consequently they represent a new phase type, and have to be designated with a new symbol H, as was also mentioned in Ref. 4.

For the substances TBNA and TBDA, having longer hydrocarbon chains, at temperatures between the existence regions of smectic C and F, new phases appeared. In the systems V and VI, these phases did not show an uninterrupted miscibility with any phase of the corresponding substance TBPA. Therefore, these phases do not belong to the smectic types G, F, C, or A. Because of the existence of the H phase as a low temperature modification to the G and F phases, an identification with the new (H) phase can also be excluded.

Meanwhile, other substances with phases of this type have been found.[3,17-19] No uninterrupted miscibility with B phases could be found.

In a series of publications (see Refs. 10, 20) Goodby, Gray *et al.* have proved miscibility relations also including the members TBBA and TBPA of the TBAA series. Besides the system TBBA-TBPA (see system II), they used binary systems combining these two substances (especially TBBA) with the 4-[2′-methylbutyl]phenyl esters of 4′-*n*-alkyloxybiphenyl-4-carboxylic acids and 4′-*n*-alkylbiphenyl-4-carboxylic acids. In the homologous series of these classes, they found F, G, and H phases, and in some special members B and E phases, too. With respect to TBBA and TBPA, their results on miscibility are in full agreement with our results.

Though there is no contradiction in the experimental results, an exchanged designation for G and H phases has been used. As mentioned above, our denomination of phases starts with PPOP as a standard for F and G phases. Goodby and Gray also use PPOP as a standard for F, but not for G phases. They designate in TBBA a phase H, which follows the smectic C phase with decreasing temperature, and use this phase as a standard in miscibility experiments (see also Ref. 21). Consequently they code the phase, which follows this H phase at lower temperature as a G phase. Therefore, the designation of all G and H phases is exchanged.

In order to avoid this confusing situation, which does not imply different physical facts, the authors (Demus, Goodby, Gray, and Sackmann)[22] agreed to use in future the designation G in the standard substance PPOP and to code the phase which follows at lower temperature as an H phase. This designation is also used in this work.

4.2 Polymorphism and structure

4.2.1 Polymorphism and the sequence rule in the TBAA series The results of the miscibility investigations in the TBAA series are summarized in Figure 1, which shows the polymorphism in the single members of the series.

The following variants occur:

N
H G C A N
H G F C A N
H G F C A
G F I C A

The H phase appears only as a stable phase in the member $n = 3$; the higher homologues possess only metastable H phases.

There is some accordance with the transition temperatures given in Ref. 6 with respect to the phases N, A, C, and the phases now designated G and H. But the existence of the F phase could only be observed in the member $n = 5$, and no I phases were found.

All the variants of polymorphism found in the TBAA series can be derived from a sequence

H G F I C A N

through the absence of one or several phases in single members.

4.2.2 Structures and phase types Besides the N phases and the known group with the phases A and C, the ordered phases H G F I could be separated. This was first begun by comparison of the transition heats in the TBAA system measured by Wiegeleben *et al.*[8] The transitions G/C, F/C, and I/C were in the order of magnitude 3000 to 7500 Joule/mol, whereas the transitions within the groups H/G, G/F, and F/I possessed smaller transition enthalpies with a highest value of 1280 Joule/mol. A further subdivision was possible, which related to the group of G, F, and I phases. The transition enthalpies between these phases amounted to less than 100 Joule/mol.

With respect to structure, the extensive investigations of Doucet *et al.*[5] on TBBA have to be mentioned first (see also Ref. 23). The phases V and VI now have to be coded as G and H phases, both possessing a layer structure with tilted molecular long axes.

In the G phases, there is a pseudo-hexagonal arrangement of the long axes of the molecules with a local herring-bone order within the layers. The first powder X-ray pattern of a G phase in PPOP, as well as the interferences in all G phases of the TBAA series[7] and also the G phases of the series of 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkyloxyphenyl]pyrimidines[24] can now be indexed by analogy with the G phase of TBBA.

With respect to the H phases, a similar behavior can be expected. The structure of this phase in TBBA (phase VI in Ref. 5) is a tilted layer structure with an order of the herring-bone type within the layers. This structure could be obligatory for all the phases of this type. The results of Leadbetter *et al.*[25] found for the H phase (named G by the authors) of TBPA are a first indication that this is the case.

The tilted layer structure for all F phases according to the initial phase of this type in PPOP was recognized by Diele *et al.*[7,24] Leadbetter *et al.*[25] proved the existence of a regular hexagonal packing of the molecules with tilted axes in the layers of the F phase of TBPA.

The I phases of TBNA and TBDA also possess layer structures with a tilt of the molecular long axes to the layer normal.[7] Meanwhile the I phase of *n*-pentyl 4-[4-*n*-dodecyloxybenzylideneamino]cinnamate has been investigated by X-rays.[26] A pseudo-hexagonal packing of the molecules has been found with a special reciprocal orientation of the central part of the molecules and the hydrocarbon chains. But the transferability of this suggested structure of the I phases of the TBAA series has not been proved so far.

If we may generalize about these tentative, fragmentary results, a phase H with a herring-bone arrangement in the layers is separated from a group of phases with a pseudo-hexagonal arrangement of the tilted molecular long axes in the layers (G, F, and I phases). This would correspond to the calorimetric behavior of the phase transitions mentioned above.

As can be seen, no clear distinction between the structures of G, F, and I phases is possible today. This may finally be found in the degree of local order and the correlation between the layers, as well as in special factors relating to molecular conformation.

4.2.3 Remarks on the coding of phases as symbols of the structure Because of the results on miscibility in system X, the problem of the existence of phases of the same phase type B by miscibility, but having different structures vanishes. The earlier designation of a phase B in TBBA with a tilted structure (B tilted, B_C, B_H) permitted a distinction from the B phases with a normal structure (B_{normal}, B_E). Now it is possible to use the symbol G as a phase type symbol, as well as a symbol of a layer structure of the type of the G phase of TBBA. The symbol B is reserved for phases which are connected by miscibility with the B phases of EEBC and possessing a hexagonal layer structure with perpendicularly oriented axes. With respect to the use of the symbols G and H, see section 4.1.

Doucet *et al.*[5] have investigated a further phase (phase VII) in TBBA appearing at lower temperatures. According to the sequence rule and the X-ray measurements (tilted layer structure) this phase should belong to a new phase type. Recently Barrall *et al.*[27] also found a phase at lower temperatures, which they coded as a K phase.† The correlation (miscibility and structure) between these phases should be awaited before coding phase VII of TBBA.

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† At the Eighth International Liquid Crystal Conference in Kyoto, it was however suggested in papers by Gray and by Leadbetter that the K phase may be a crystal modification. Further experimental work is therefore needed here.

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