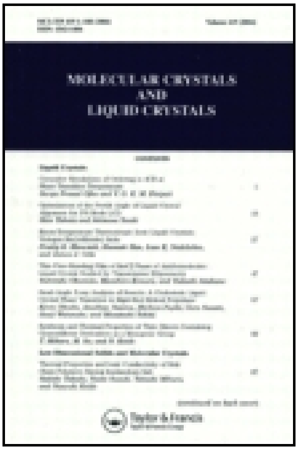

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Polymorphism in the Homologous Series of the 2-[4-n-Alkylphenyl]-5- [4-n-alkyloxyphenyl]pyrimidines

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Polymorphism in the Homologous Series of the 2-[4-*n*-Alkylphenyl]-5-[4-*n*-alkyloxyphenyl]pyrimidines†

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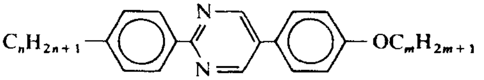
Several members of the homologous series of 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkyloxyphenyl]pyrimidines



have been synthesized. The phase transitions were determined by microscopic and calorimetric investigations. The classification of the smectic modifications was done by investigation of the miscibility relations and by texture observations. Besides the nematic phase and smectic phases A and C, smectic phases F, G and H were observed. All the variants of polymorphism observed can be derived from the sequence H G F C A N.

1 INTRODUCTION

Some years ago, the synthesis and investigation of the smectic tetramorphous compound 2-[4-*n*-pentylphenyl]-5-[4-*n*-pentyloxyphenyl]pyrimidine were published.[1] Besides the smectic A and C phases, two other liquid crystalline phases were found. Because of the textures and the results of X-ray investigations, these phases were recognized as new smectic phases F and G.

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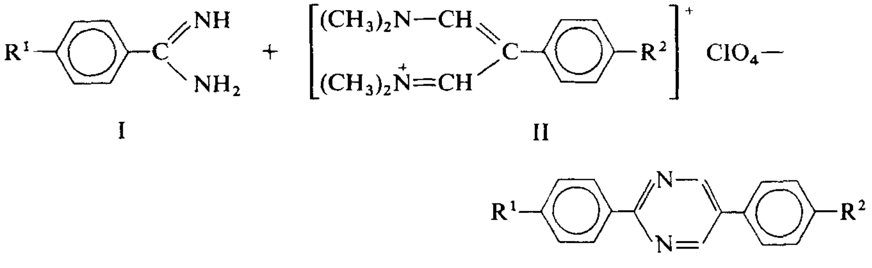
† Paper No. 24 in the series "Relations of isomorphism between liquid crystalline phases."

In another paper,[2] other substances with G phases were described. In the Halle Liquid Crystal Group, a variety of substances were later found which also possess F and G phases (see Ref. 3 and summarizing conference reports).[4,5] The detailed description of these results starts with the investigations of the textures and the miscibility relationships in the homologous series of 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkyloxyphenyl]pyrimidines. The X-ray investigations and the calorimetric measurements have already been published.[6,7]

2 SYNTHESIS

Using the previously described methods for the synthesis of pyrimidine derivatives,[1] we prepared the pyrimidines (III) in high yields and good purity by cyclization of the 4-*n*-alkylbenzamidine hydrochlorides (I)[8] using the alkyloxy-substituted trimethine salts (II) in the presence of sodium methoxide.



R^1 = alkyl
R^2 = alkyloxy

We obtained the trimethine salts (II) in very good yields starting from the substituted phenylacetic acids and using a Vilsmeier–Haak-reaction.[9,10,11] In detail, the synthesis of the 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkyloxyphenyl]-pyrimidines may be accomplished according to the following instructions:

The trimethine salt (0.01 mol) and the amidine hydrochloride (0.015 mol) were solved in absolute methanol (50 ml). During stirring at room temperature, a solution of sodium methoxide (0.69 g, 0.03 mole) in absolute methanol (25 ml) was added slowly. After heating under reflux for six hours the mixture was cooled, the precipitate was filtered off, and washed with water and several times with ethanol. The product was crystallised several times from a mixture of benzene and ethanol till a constant clearing point was obtained. The yields were found to be 80–95%. Within the limits of error, the results of analysis for C, H, and N agreed with the calculated values.

3 TRANSITION TEMPERATURES AND PHASE TYPES

The transition temperatures were determined by means of a polarising microscope equipped with a heating stage, and also by using a Perkin–Elmer Differential Scanning Calorimeter (DSC 1–B resp. DSC 2). The temperature at the maximum of the transition peaks was chosen as the actual transition temperature.

The values are listed in Ref. 7, together with the enthalpies of transition. There are two groups of pyrimidines. The first group contains side chains with equal numbers of carbon atoms, and the other group consists of homologues of the pentyloxyphenyl compound (5/05) obtained by variation of the alkyl-phenyl chains (the compounds *n*/05).

In the Figures 1 and 2, the trends of the transition temperatures in these series are shown. They confirm the existence of phases which belong to the common phase types which are characterized by the letters shown. The assignments to the phase types shown have been made by investigations of the miscibility relations and by comparisons of the textures (see sections 4 and 5).

The compounds 5/05 and 4/04 (Figure 1) each possess a further smectic phase below the G phase in the supercooled region. Therefore they represent compounds which show the phase type H which also occurs amongst the low temperature smectic phases of the terephthalylidene-bis-[4-*n*-alkylanilines] (see Refs. 3, 4, 5 and the next communication in this series).

Besides the transitions between liquid crystalline phases, the existence of extensive polymorphism in the solid state was proved. The results will be published separately.[7,12]

4 TEXTURES

The textures of the smectic modifications A, C, F, and G have been described for the standard compound 5/05.[1] Considering the fact that now additional peculiarities have been found, the textures will be treated again here. Starting from the crystalline state, with increasing temperature during the first heating cycle, all the liquid crystalline modifications occur with paramorphotic textures which are not characteristic.[13]

Starting from a simple fan shaped texture of smectic A (Figure 3), with decreasing temperature and *before* reaching the phase transition to smectic C, some additional discontinuities similar to those in broken fan-shaped textures, appear (Figure 4). These discontinuities grow continuously in size and contrast on approaching the transition temperature. On reaching the transition temperature (which is known from the calorimetric experiments), many further discontinuities, possibly comparable with the zig-zags in simple

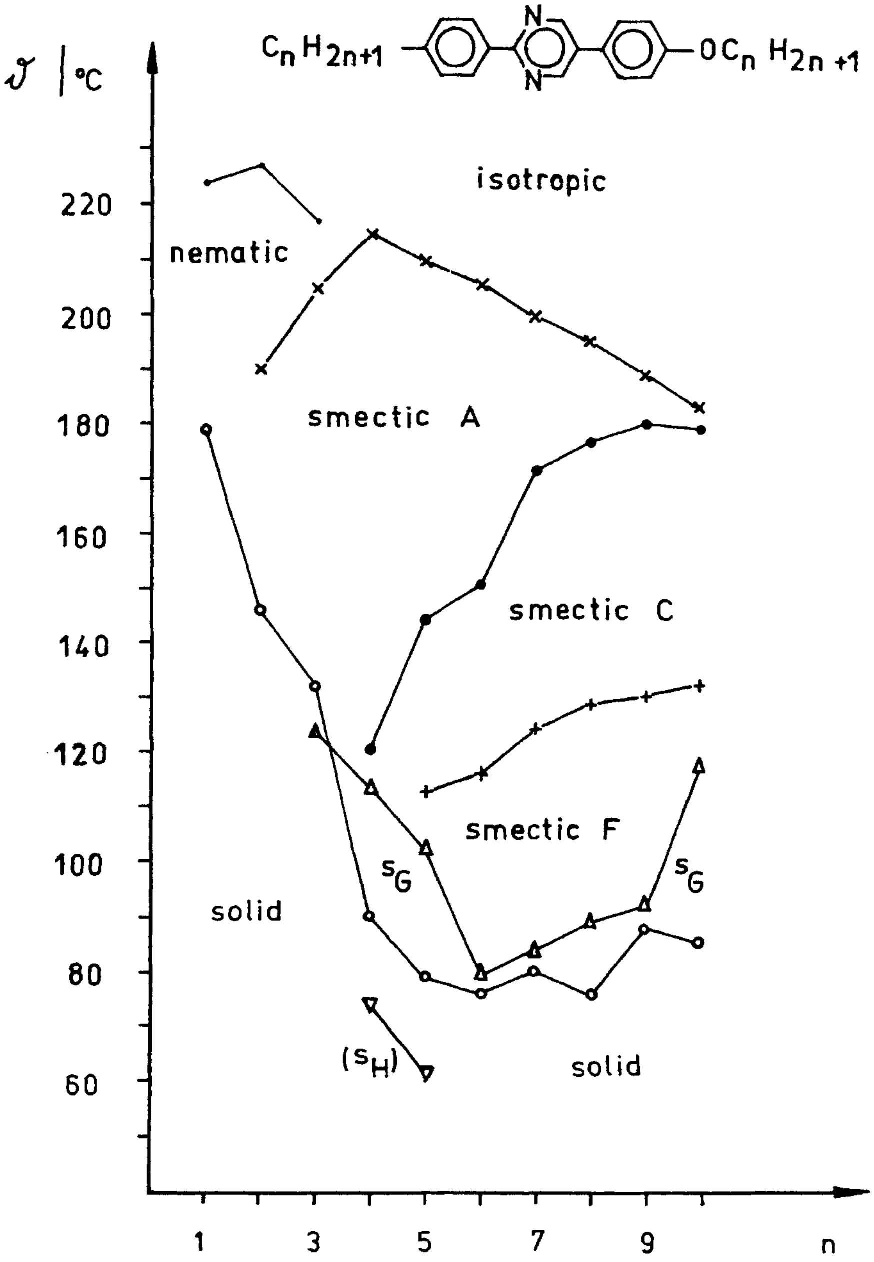


FIGURE 1 Phase transition temperatures for the series (*n*/0*n*).

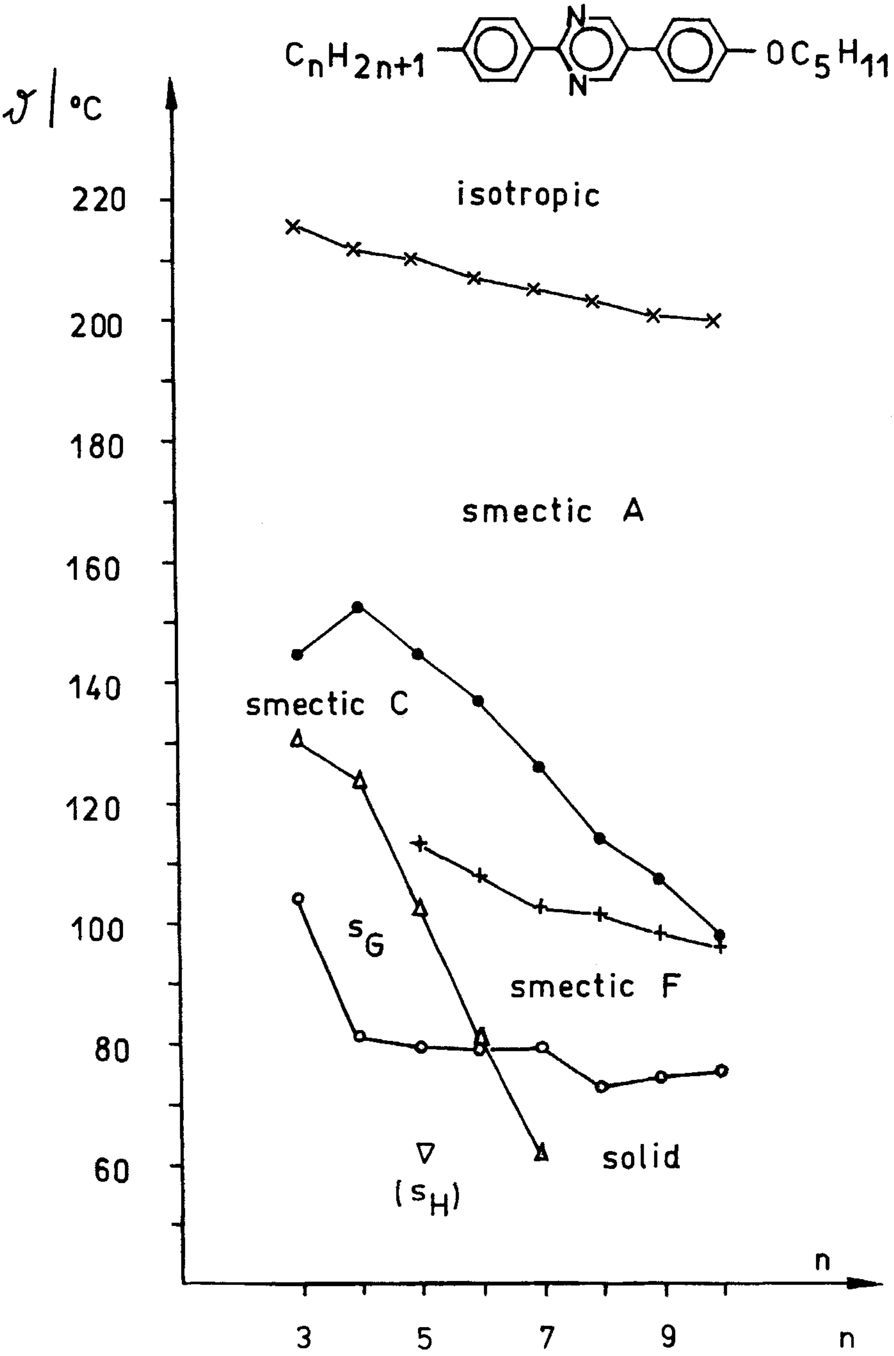


FIGURE 2 Phase transition temperatures for the series (*n*/05).

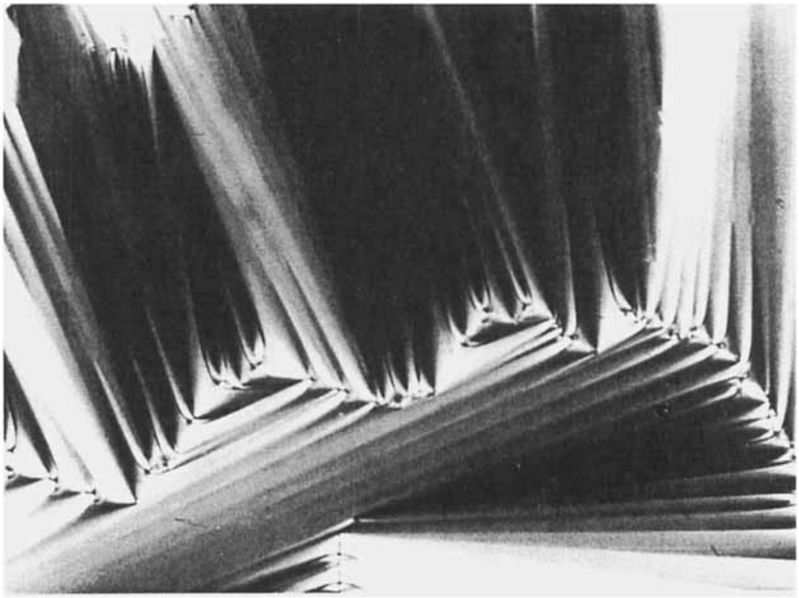


FIGURE 3 2-[4-*n*-Pentylphenyl]-5-[4-*n*-pentyloxyphenyl]pyrimidine (substance No. 7). Smectic A, fan-shaped texture, 180°C, ×250.

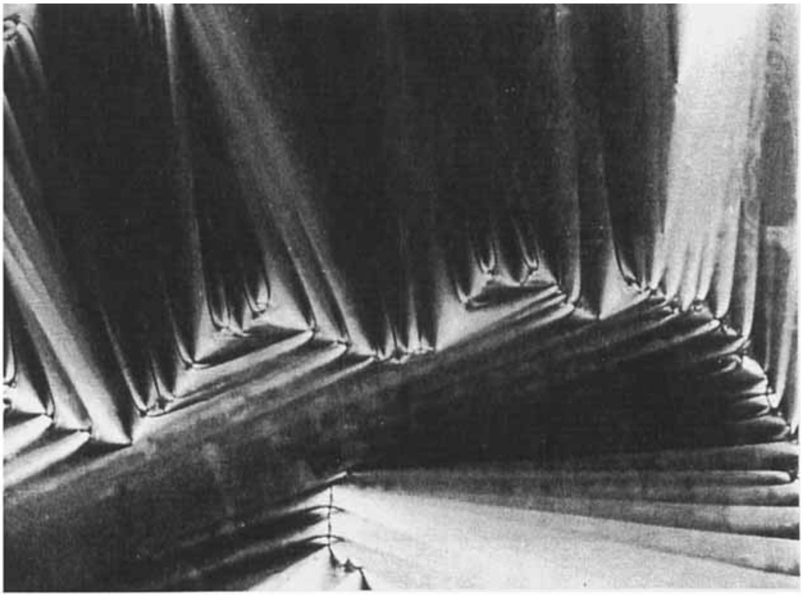


FIGURE 4 Substance No. 7. Smectic A, fan-shaped texture, 150°C, × 250.

focal-conic textures,[14] appear (Figure 5). These zig-zags are interpreted as sets of alternating $+\pi$ and $-\pi$ disinclinations in layer structures. The optical phenomena described go on nearly continuously, and therefore the determination of the transition temperature S_A/S_C in preparations with the fan-shaped texture is difficult. Cooling the preparation down to the temperature range of the smectic *F* phase yields the striped, broken, fan-shaped texture (Figure 6). This texture exhibits characteristic sets of fine stripes which are concentric arcs perpendicularly cutting the hyperbolae of the fan-shaped textures. After the transition to smectic G, a characteristic mosaic texture (Figure 7) is adopted which clearly shows paramorphotic features of the foregoing fan-shaped textures. By cooling slowly, the texture changes after some time to a mosaic texture with larger domains (Figure 8). On heating the preparation again, the textures of the smectic F, C, and A phases are similar to those in Figures 3 to 6, although in the smectic F texture, the stripes may then be broader (Figure 9) than those in the initial smectic F texture (Figure 6). This points to the fact that the breadth of these stripes is not characteristic of the substance, but depends on the conditions of preparing the sample.

Because of the occurrence of paramorphosis in the higher homologues (especially n, m = 8, 9, 10), in the case of fan textures, only small differences exist between the textures of smectic G, F, and C. Therefore the recognition of the phase transitions and the exact establishment of the transition temperatures are extremely difficult when using preparations with fan textures.

A better way for studying the phase transitions is to start from homeotropic preparations of the smectic A phase. After cooling, smectic C appears in the planar orientation, giving the schlieren texture (Figures 10) at exactly the same temperature as that which corresponds to the maximum in the thermogram obtained from the DSC method. The smectic C schlieren texture is somewhat blurred, and the dark schlieren themselves are narrow compared with those of the smectic texture (Figure 11). The texture of the smectic G phase obtained from this smectic phase is shown in Figure 12 and has more mosaic-like characteristics.

5 MISCIBILITY

In the following diagrams, certain abbreviations are used: Cl.p. clearing point; tr. transition temperatures between liquid crystalline phases; m.p. melting point. The numbers within the diagrams refer to extreme temperatures in the transition curves or to the temperature of a three phases equilibrium.

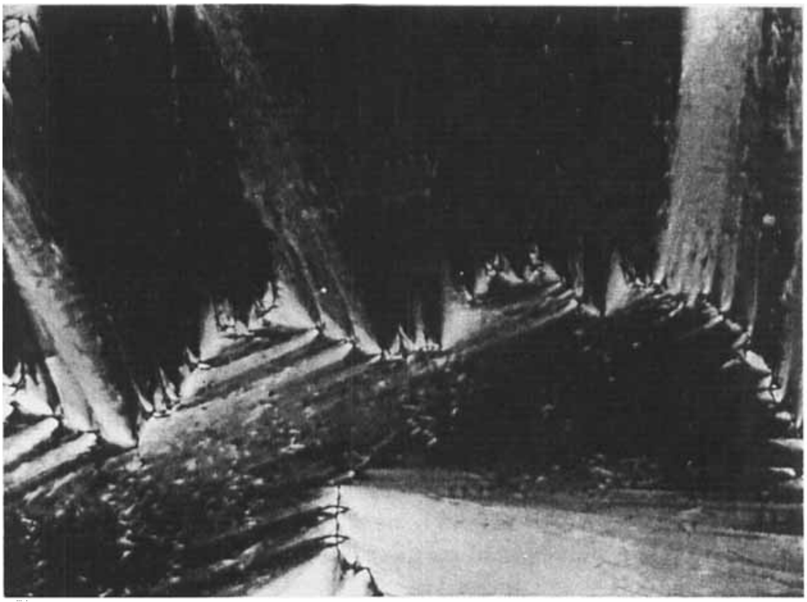


FIGURE 5 Substance No. 7. Smectic C, broken fan-shaped texture, 131°C, × 250.

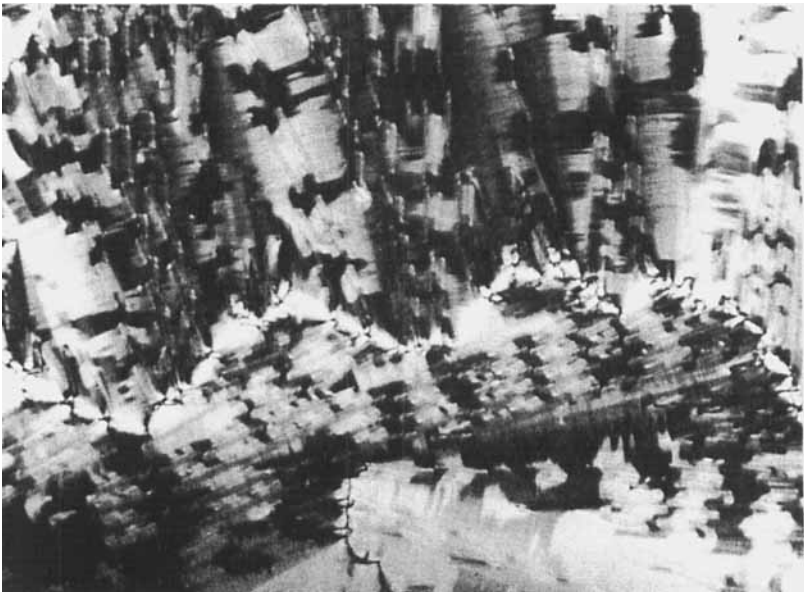


FIGURE 6 Substance No. 7. Smectic F, striated, broken fan-shaped texture, 107°C, × 250.

FIGURE 7 Substance No. 7. Smectic G, paramorphotic mosaic texture, 90°C, × 250.

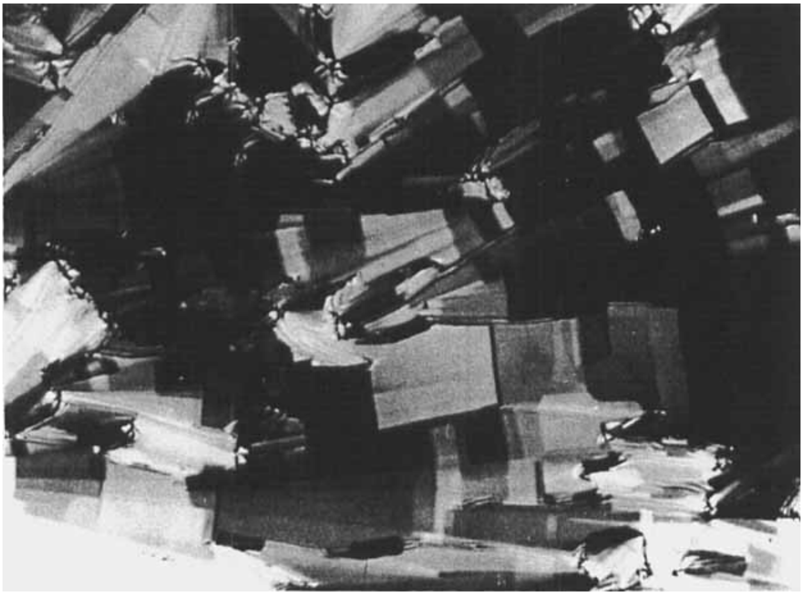


FIGURE 8 Substance No. 7. Smectic G, mosaic texture, 85°C, × 250.

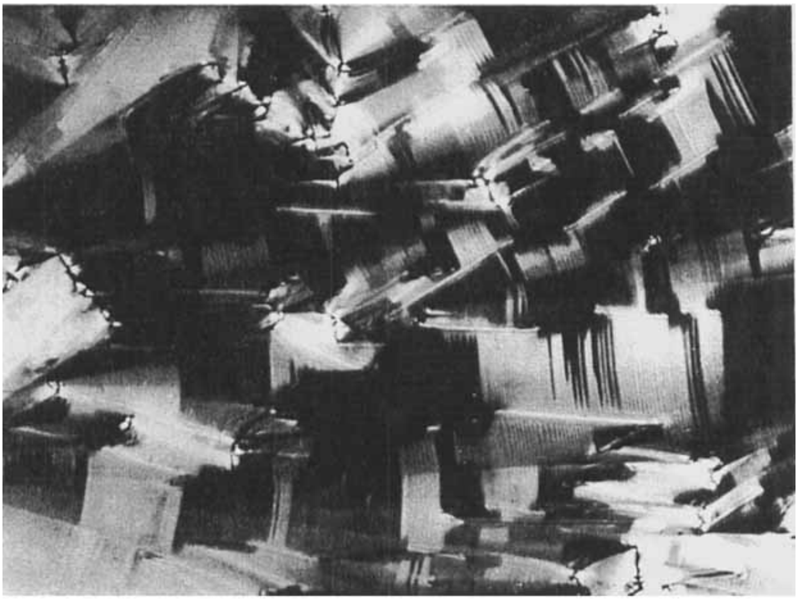


FIGURE 9 Substance No. 7. Smectic F, striated fan-shaped texture, 105°C, × 250.

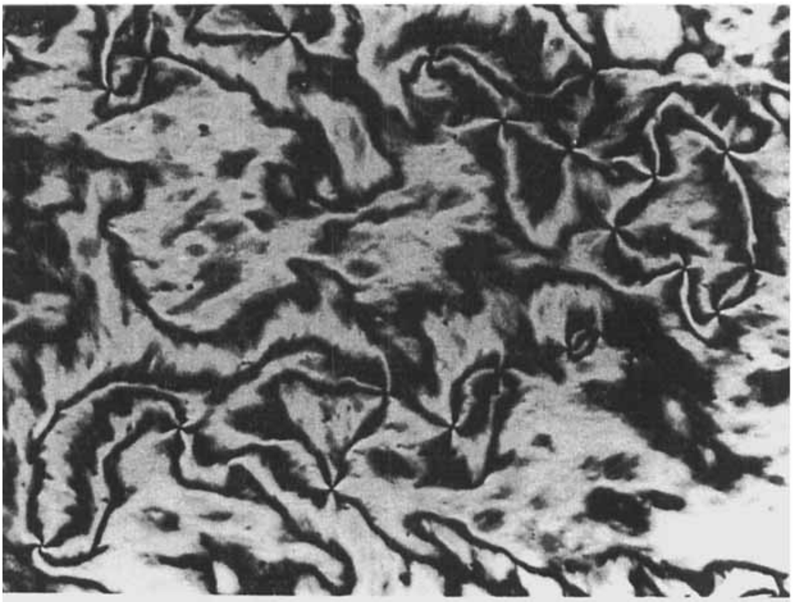


FIGURE 10 Substance No. 7. Smectic C, schlieren texture, 131°C, × 250.

FIGURE 11 Substance No. 7. Smectic F, schlieren texture, 107°C, × 250.

FIGURE 12 Substance No. 7. Smectic G, paramorphotic "mosaic" texture, 85°C, × 250.

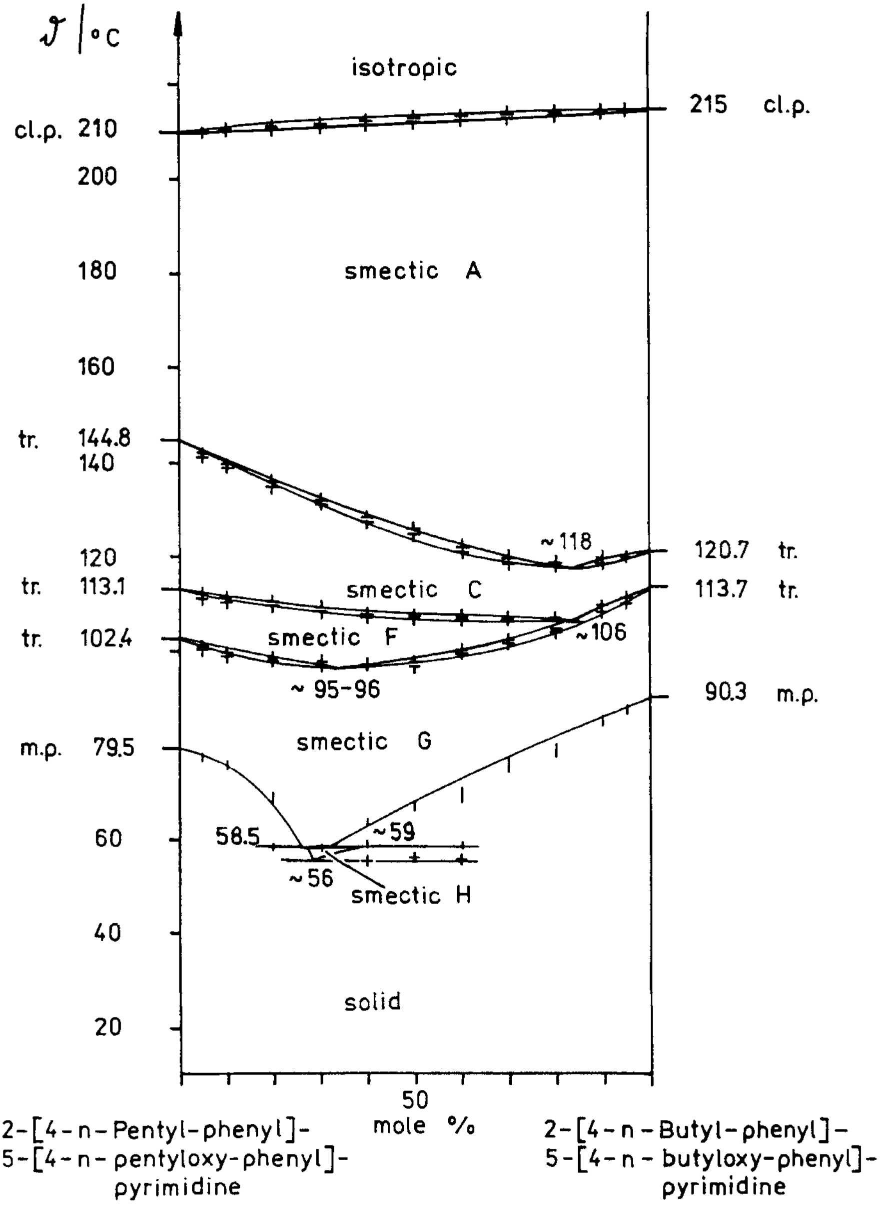


FIGURE 13 System (5/05–4/04). a) stable part.

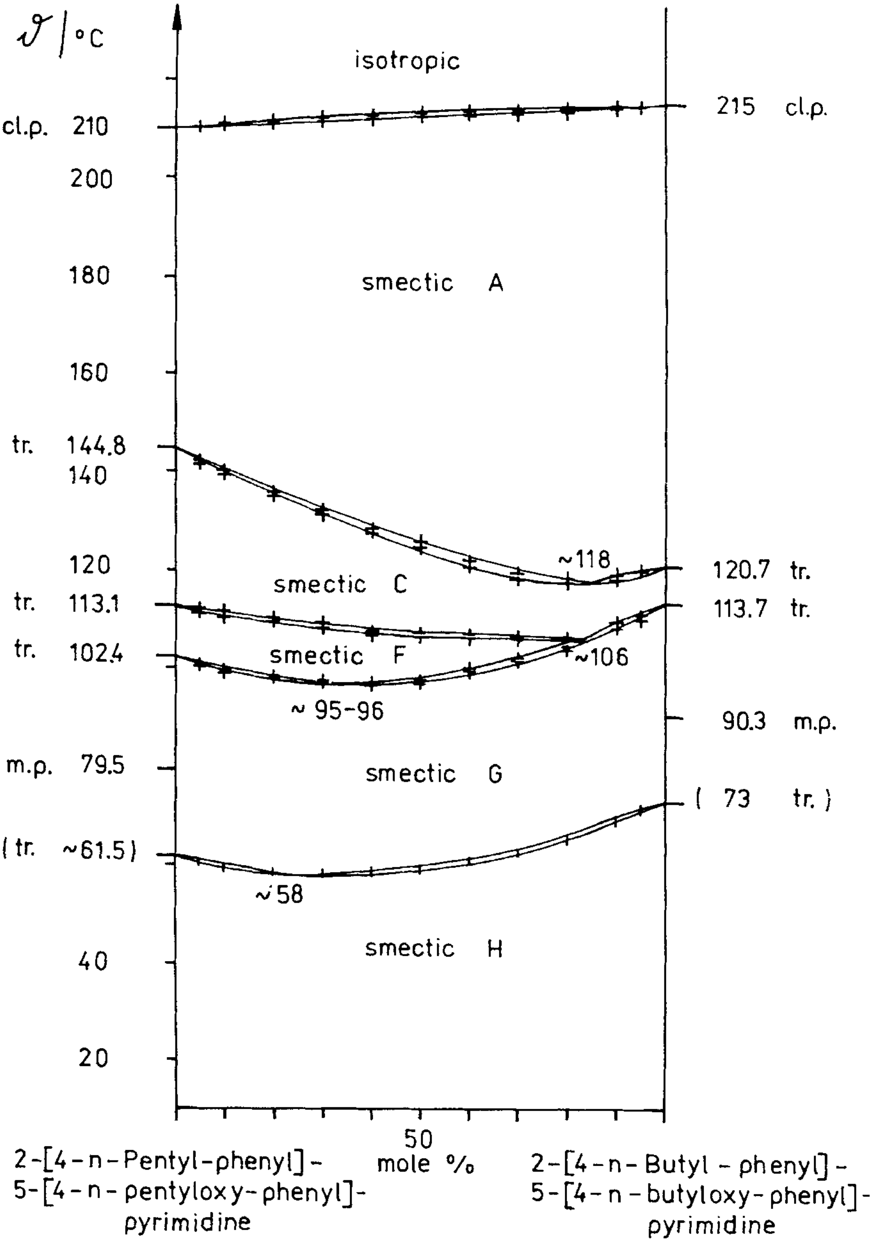


FIGURE 13 b) diagram including metastable regions.

Figures 13–19 show the miscibility relations between the phases of some homologues in binary systems. As usual,[13] a first survey of the diagrams was obtained by the contact method and this was completed by the investigation of single preparations with different compositions. Starting from the compound 5/05 as the standard substance, the phase types of the smectic phases of the other compounds were determined by the criterion of complete miscibility.

The binary system 5/05–4/04 (Figure 13) has already been investigated (see Figure 1 in Ref. 2). Due to the latest miscibility relations established between terephthalylidene-bis-[4-*n*-butylaniline], as well as its higher homologues, and the pyrimidines 5/05 and 4/04, we have found additionally a smectic H modification in the supercooled region of these pyrimidines.[3,4,5] Therefore, a reinvestigation of the published system (Figure 1 in Ref. 2) with the newly synthesised reference substance 5/05 was made. Figure 13 shows the new results. Good agreement in the thermodynamically stable regions of the diagrams of state (Figures 13(a) and (b)) exists. Additionally, we could confirm complete miscibility between the two metastable H phases (Figure 13(b)). Only a small stable H phase region seems to occur near the eutectic point (Figure 13(a)). Possibly detailed reinvestigations of the miscibility between the pyrimidines 5/05 and 4/04, resp. and the higher homologues of the pyrimidines may reveal further metastable H phases. In Figure 19(a) and (b), the existence of a metastable G phase in the compound 3/03 can be seen within the new phase sequence G A N.

These results may be compared to the behaviour of the transition temperatures in the homologous series of the Figures 1 and 2. The trends of the temperatures in these series together with the texture observation support the classification of the smectic phases derived from the miscibility investigations.

6 DISCUSSION

The liquid crystal polymorphism in the homologous series of the pyrimidines described follows the sequence rule[13] applied to the general sequence H G F C A N. All existing variants of polymorphism may be derived from this sequence by subtracting one or more of the phases. According to Figures 1 and 2, the following variants occur:

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

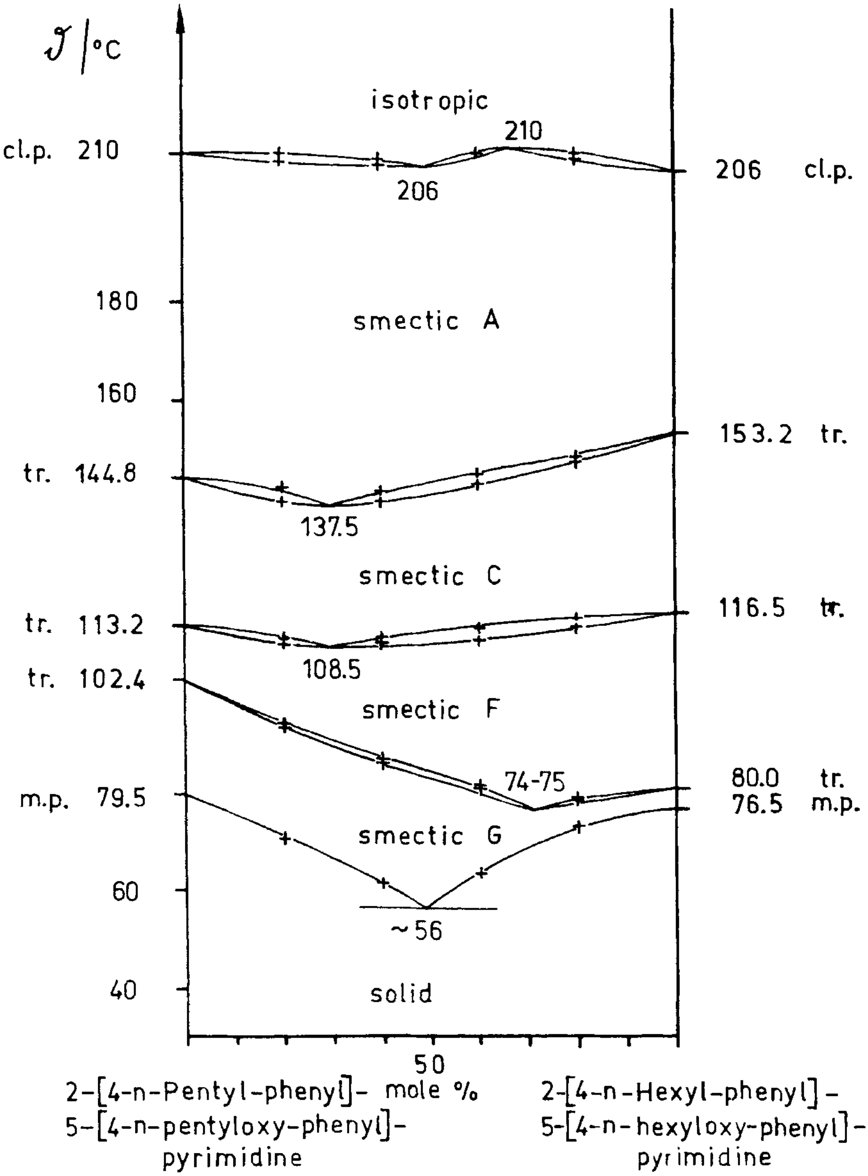


FIGURE 14 System (5/05–6/06).

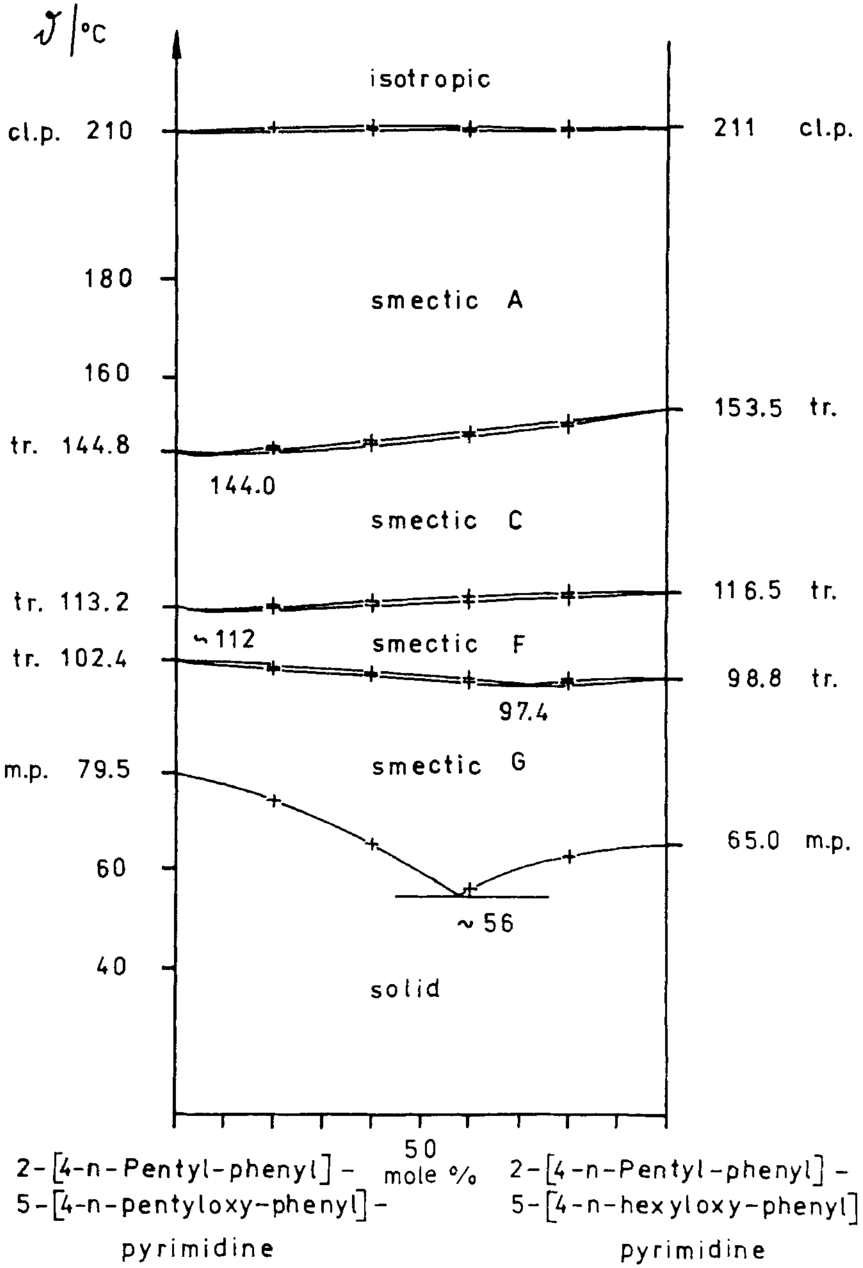


FIGURE 15 System (5/05-5/06).

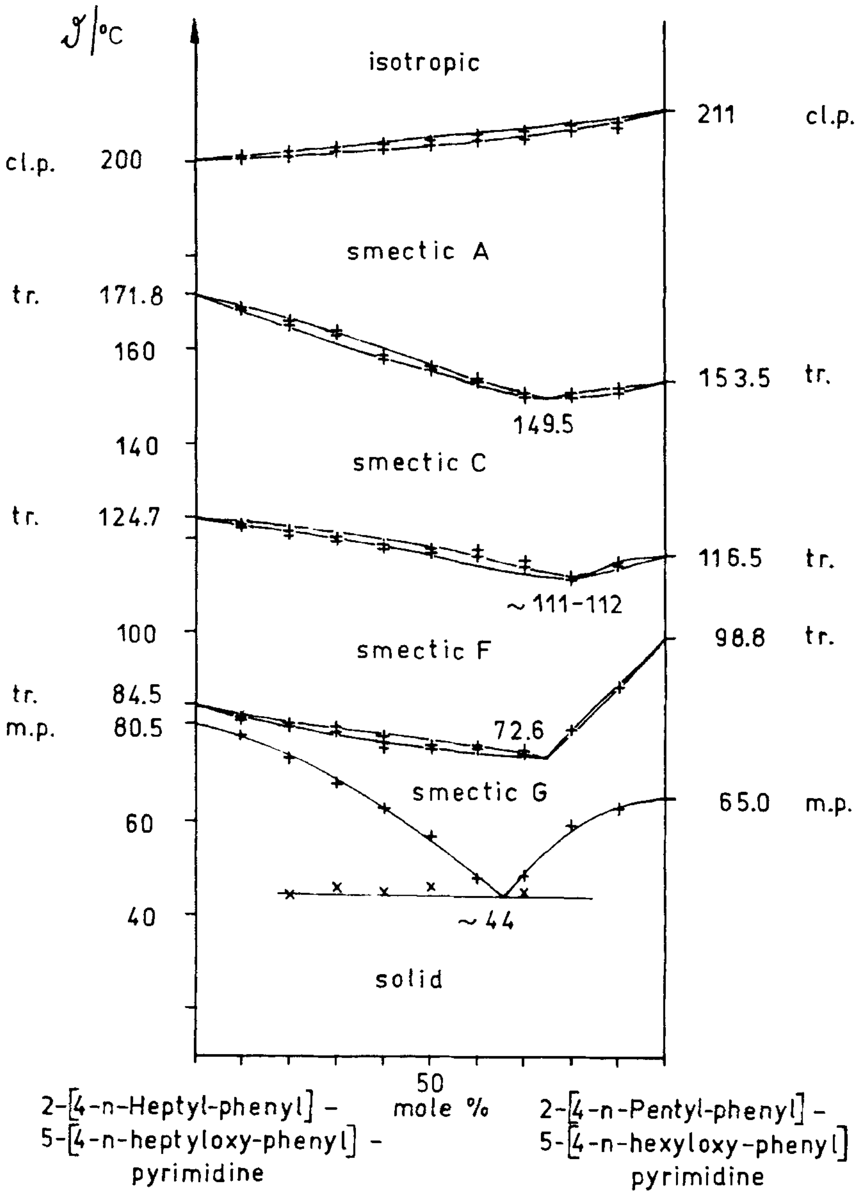


FIGURE 16 System (7/07-5/06).

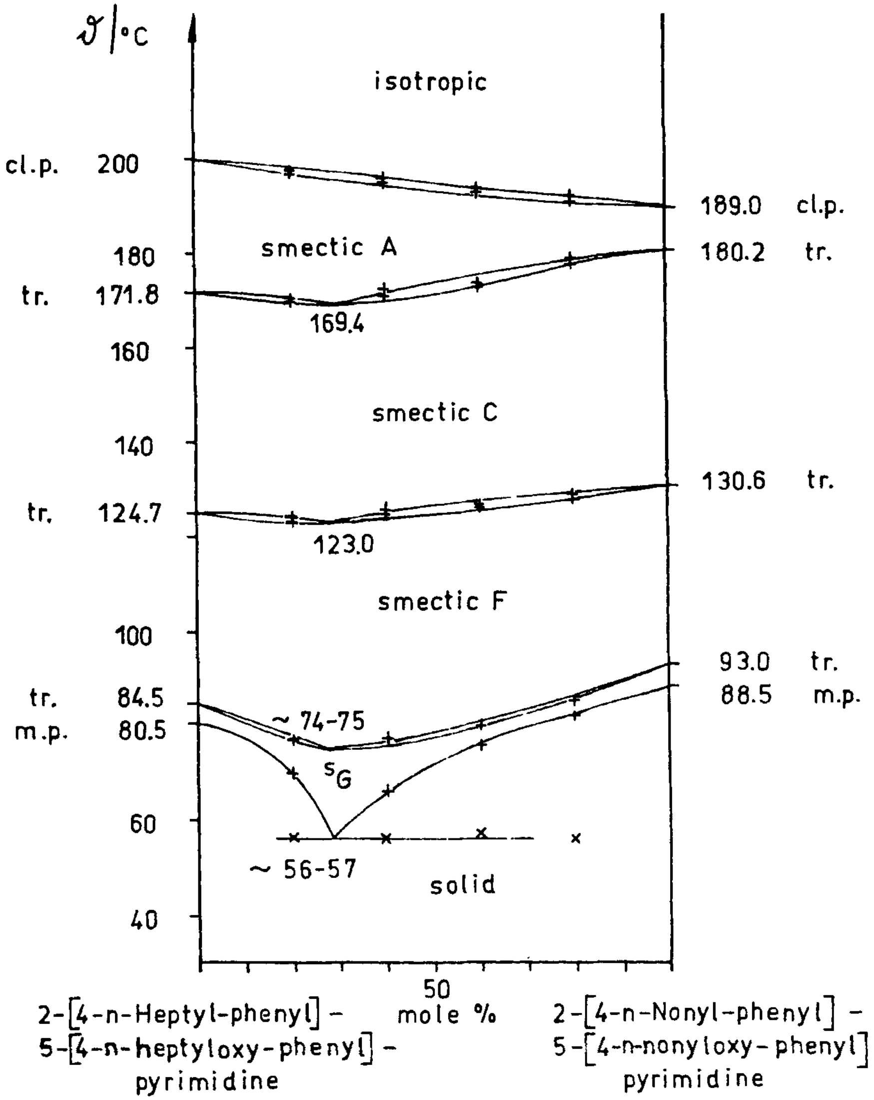


FIGURE 17 System (7/07–9/09).

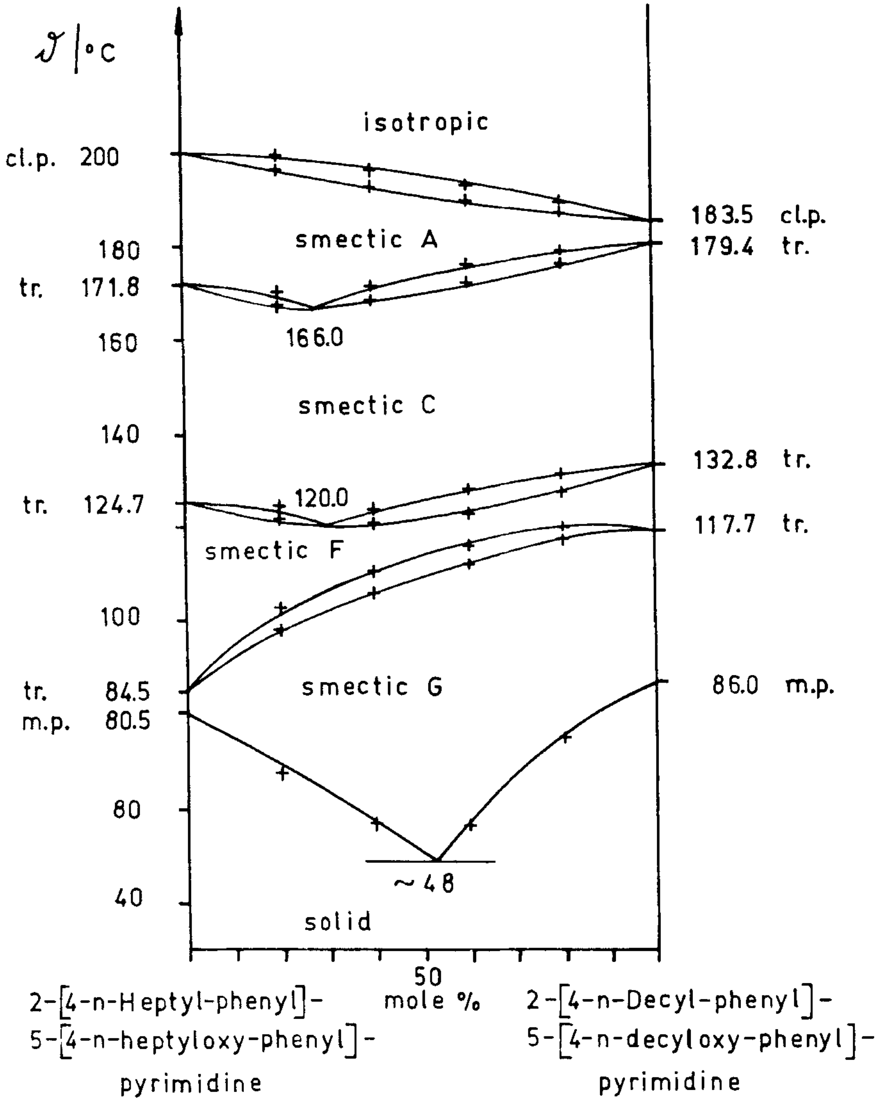


FIGURE 18 System (7/07–10/0 10).

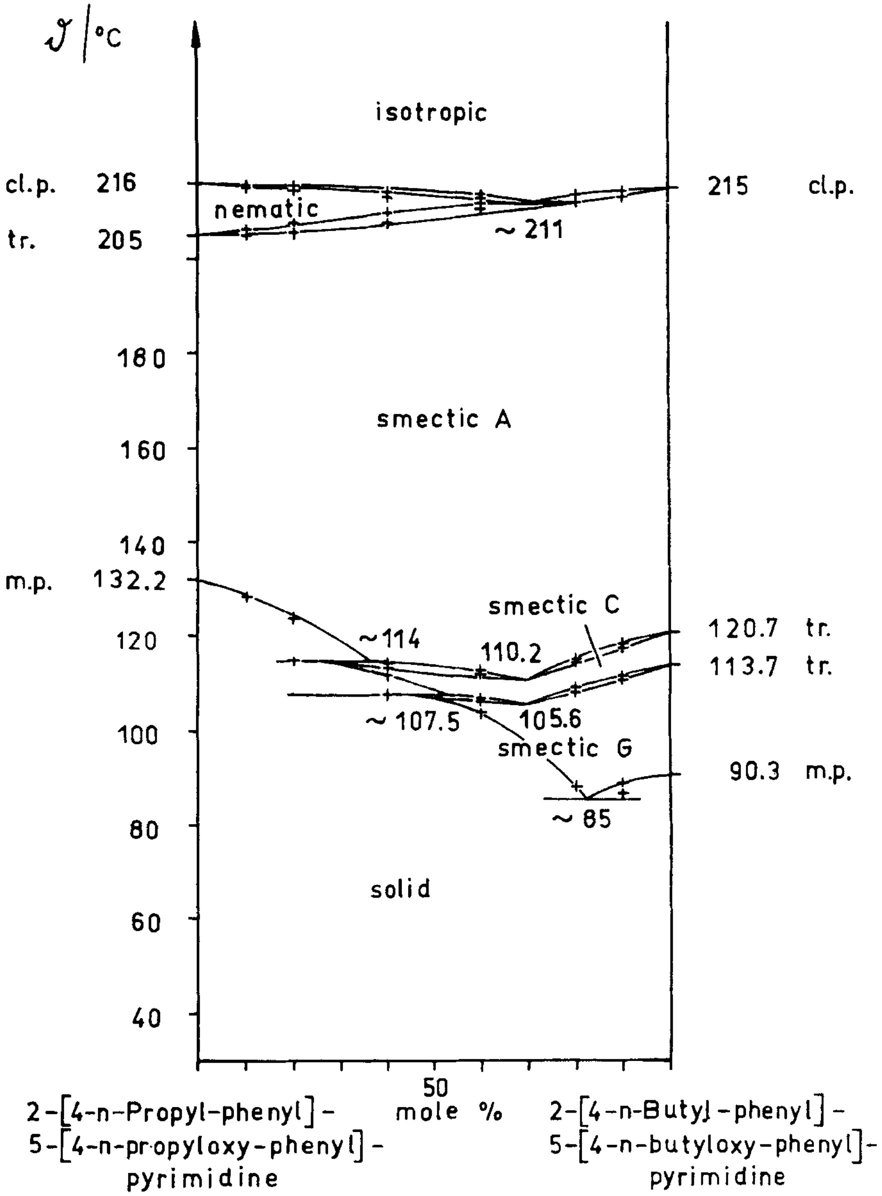


FIGURE 19 System (3/03–4/04). a) stable part.

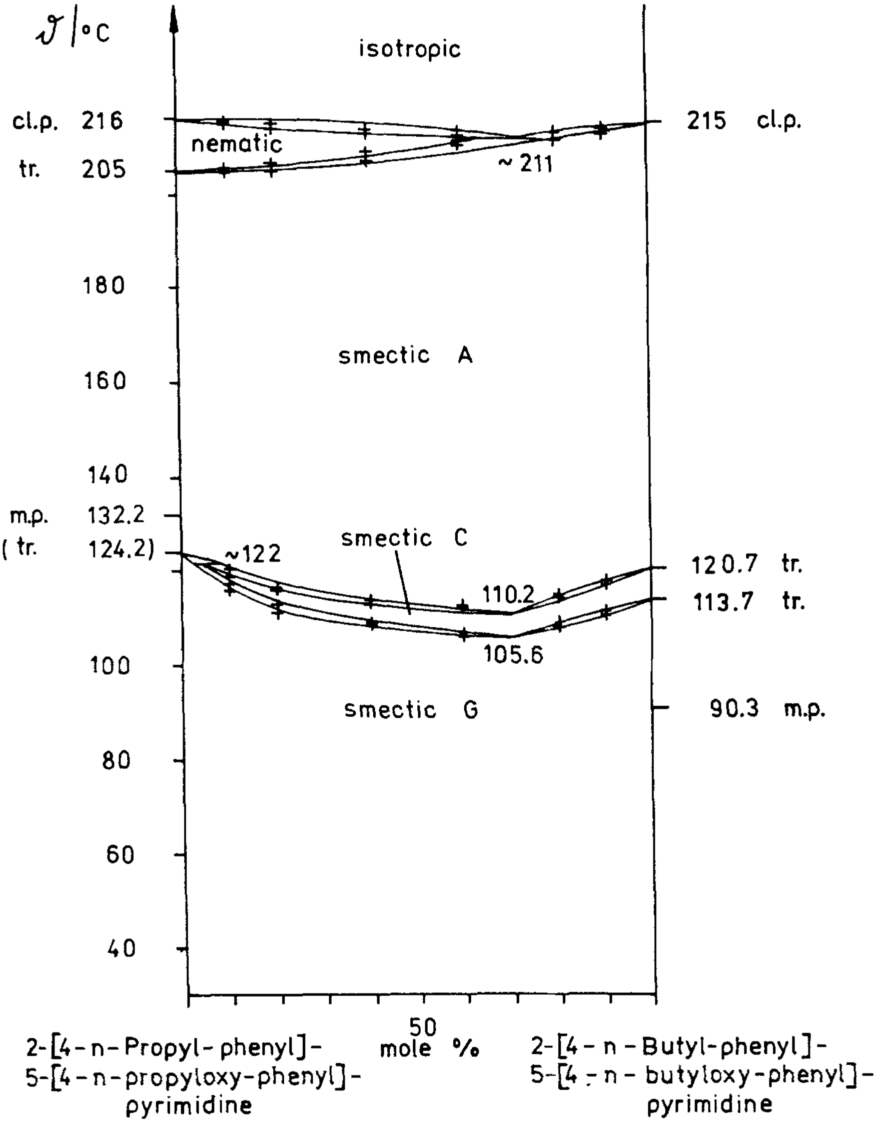


FIGURE 19 b) diagram including metastable regions.

In Reference 6, X-ray investigations of members of the homologous series displayed in Figure 1 have been published. All the smectic phases possess a layer structure. The long molecular axes are tilted with respect to the layer planes in the C, F and G phases. The reflections obtained from the G phases can be indexed on the assumption of a monoclinic cell. The indices show a characteristic trend along the series, as might be expected for phases of the same type within a homologous series. The stuctures agree with that found for phase V of terephthalylidene-bis-[4-*n*-butylaniline] (TBBA).[17] This phase was meanwhile reinvestigated by miscibility experiments and its earlier classifications as a B phase[2] must now be changed to a G phase.[3,4]

With respect to the layer thickness, the transitions G/F produce only small changes.[6] The transition heats in the series given in Figure 1 have small values for the transitions G/F (270J $\cdot$ mol^{-1} for the member 5/05) with a strongly decreasing trend along the series. The values for the F/C transitions are higher (700 J $\cdot$ mol^{-1} for the member 5/05) with a strongly increasing trend along the series.[7]

According to these results, there exists a close relationship between F and G phases. A more detailed X-ray investigation of the F phase of the 5/05 compound has recently been published in Reference 18. According to this work, a c-centered monoclinic lattice with a hexagonal arrangement of the molecules exists in the F phase.

The existence of the phases F, G, and H in other homologous series has also been reported.[19,20,21,22,23,3,4,5] This proves that the phases F, G and H are examples of general phase types. The comparison of these results with those for the homologous series of terephthalylidene-bis-[4-*n*-alkyl-anilines] will be discussed in a following paper.

Acknowledgement

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