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SMECTIC F PHASES IN THE TEREPHTHALYLIDENE-BIS-4-n-ALKYLANILINES

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Abstract Recently terephthalylidene-bis-4-n-pentylaniline (TBPA) was reported to have two types of tilted smectic B (smectic H) phase. However, our study of this material shows that this compound has a smectic F phase and a smectic H phase, and *not* two H phases as previously thought.

Introduction Recently,[1] terephthalylidene-bis-4-n-pentylaniline (TBPA) has been reported as a material that exhibits two separate and distinct tilted smectic B phases (smectic H phases). The evidence was based mainly on the co-miscibility of certain phases of this material with particular classified phases of terephthalylidene-bis-4-n-butylaniline (TBBA). We in fact obtained results from our miscibility study involving TBPA and TBBA similar to those obtained by the previous workers. However, our interpretation of the data is entirely different, and a complete analysis of the results is given in this paper.

Results and Discussion Our findings indicate that TBPA has the following phase sequence, N, S_A, S_C, S_F, S_H, S_G. Our identification of these phases is based on three systematic types of analysis, which are as follows:

(a) Microscopic Textures: On cooling the isotropic liquid of terephthalylidene-bis-4-n-pentylaniline (TBPA), a nematic phase was obtained. On further cooling, this nematic phase gave a smectic phase which exhibited two types of texture, namely the clear focal-conic fan texture and the uniaxial homeotropic texture; the fans of the focal-conic texture separated in the form of bâtonnets. The textures and flow properties of this phase indicated that it was of the A type. This fact was confirmed on further cooling, when the uniaxial phase gave rise to a tilted smectic C phase. This phase was readily identifiable from its microscopic textures. The clear fans of the preceding phase became broken and sanded in appearance, and the homeotropic texture gave rise to the typical, birefringent schlieren texture of a smectic C phase. This schlieren texture changed colour on cooling, and the areas bordered by the schlieren 'brushes' became lined, the lines of one area being at right angles to those of the neighbouring areas.[2] Such lines have been interpreted in terms of an undulation mode in the S_C layers occurring under stress (cooling). The phase also showed flow properties on displacement of the coverslip.

On further cooling, the smectic C phase gave rise to another tilted phase. This phase gave two types of microscopic texture, the broken fan texture and the schlieren texture. In the broken fan texture, the fans have a chequerboard pattern across their backs (Plate 1). The schlieren texture (Plate 2) was highly birefringent, highly coloured, and very mobile. Plates 1 and 2 can be compared with those published by Demus *et al.*[3] for the F phase of their pyrimidine compound; the textures are also similar to those obtained by us for the F phases of certain esters.[4] On further cooling, the suspected F phase gave rise to a further tilted phase which was readily identifiable as a smectic H from its microscopic textures. The phase exhibited two textures, namely the broken fan texture and the mosaic texture. Both of these textures were very typical of a smectic H phase.

On further cooling, the S_H phase gave rise to a smectic G phase. This phase change was rather more subtle; the fan texture changed very little, but the mosaic texture became crossed with a number of zig-zag lines, almost giving the impression of shark's teeth.

Therefore, if the smectic C phase and smectic H phase have been correctly identified, then the unidentified phase occurring between the two must either be of the F type or a completely new phase.

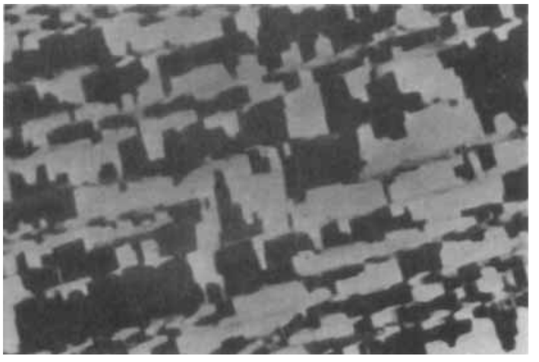

PLATE 1
The broken fan texture of the F phase of TBPA (x200)

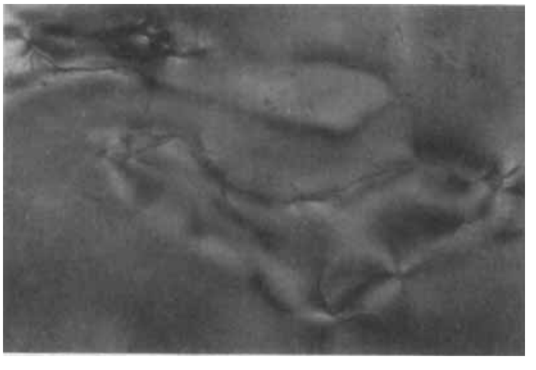

PLATE 2
The schlieren texture of the F phase of TBPA (x200)

(b) Miscibility Studies: Firstly, TBPA was shown to exhibit N, S_A, S_C, S_F, S_H, and S_G phases by their separate co-miscibility with those of the known smectic F material[4] 4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate (N, S_A, S_C, S_F, S_H, S_G) (see Fig 1).

Secondly, the results of the miscibility study which has created the confusion are shown in Fig 2. This miscibility study was carried out with TBBA (N, S_A, S_C, S_H, and S_G phases) and TBPA (N, S_A, S_C, S_F, S_H, and S_G phases). It can be seen from the graphical plot of the diagram of state that the S_C to S_F transition temperature curve and the S_F to S_H transition temperature curve approach each other tangentially as the molar amount of TBPA is decreased, thus indicating that TBBA either has latent S_F characteristics or it in fact exhibits a S_F phase of extremely short thermal range and has a S_C-S_F-S_H sequence which cannot be detected under normal conditions.

(c) Differential Thermal Analysis: Differential thermal analysis was used to confirm the transition temperatures (°C) of TBPA. These were found to be as follows:

$$I \underset{233}{\rightleftarrows} N \underset{212}{\rightleftarrows} S_A \underset{179}{\rightleftarrows} S_C \underset{149}{\rightleftarrows} S_F \underset{140}{\rightleftarrows} S_H \underset{61}{\rightleftarrows} S_G$$

melting point of solid = 68

The enthalpy values for the above transitions were determined and found to be very similar to those reported previously.[1] The relatively large enthalpy value for S_C-S_F transitions was therefore confirmed.[1,4]

Still more recently, we have prepared terephthalylidene-bis-4-n-hexylaniline and it appears that this compound also exhibits S_C-S_F and S_F-S_H transitions.

Experimental The terephthalylidene-bis-4-n-pentylaniline was prepared by standard methods. The product was recrystallised until the transition temperatures were found to be constant. Mass spectrometry and infra-red analysis confirmed the structure of the final product. Transition temperatures were determined using a Mettler FP52 hot stage and control unit. Checks on transition temperatures and measurements of enthalpies of transition were made using a Stanton Redcroft low temperature differential thermal

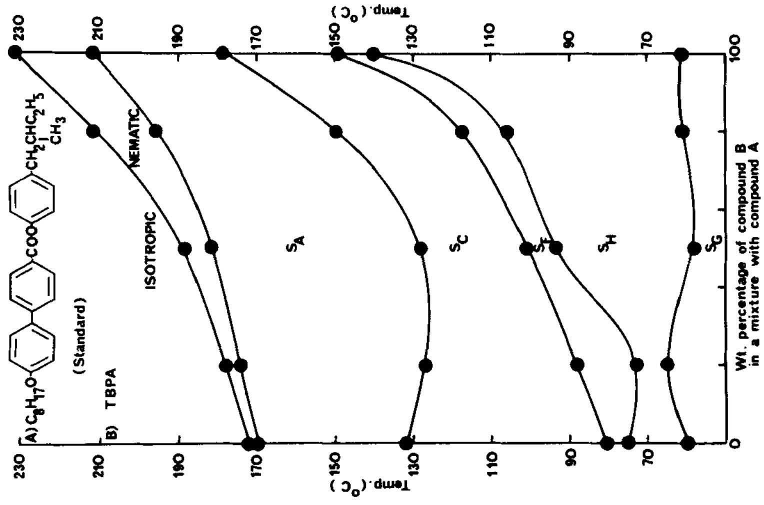

FIGURE 1

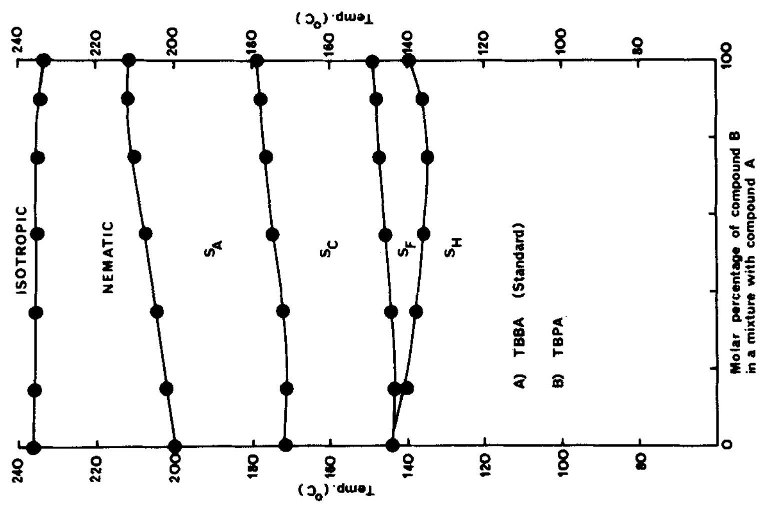

FIGURE 2

analyser (model 671B).

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