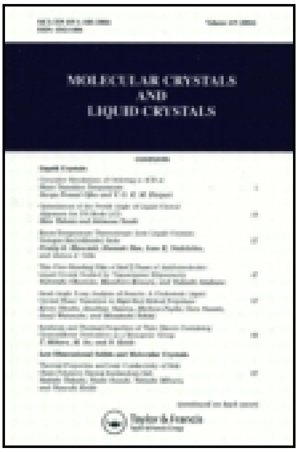

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Pressure Induced Twist Grain Boundary Phase

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PRESSURE INDUCED TWIST GRAIN BOUNDARY PHASE

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Abstract We report high pressure studies on a binary system of 4-(2'-methyl butyl)phenyl 4'-n-octyl biphenyl-4-carboxylate (CE8 from BDH) and 4-n-dodecyloxy biphenyl-4'-(2'-methyl butyl)benzoate (C12). For the concentration range $0.32<X<0.62$, where X is the weight fraction of C12, the system shows the following sequence of transitions at room pressure: Isotropic-Cholesteric (Ch)-Twist Grain Boundary (TGB)-Smectic A (A)-Smectic C* (C*). For X=0.25, the Ch phase transforms directly to the A phase at 1 bar, but there is an induced TGB phase between the Ch and A phases at elevated pressures. Analysis of the topology of the pressure-temperature diagram in the vicinity of the Ch-TGB-A meeting point indicates that is a critical end point rather than a bicritical point as expected from the mean field theory. At X=0.64 there is a direct TGB-C* transition at 1 bar, but there appears a pressure induced A phase between the TGB and C* phases. The topology of the phase diagram suggests that the TGB-A-C* meeting point is a bicritical point.

INTRODUCTION

In a previous communication[1] we presented the temperature-concentration (T-X) phase diagram of binary system of 4-(2'-methyl butyl)phenyl 4'-n-octyl biphenyl -4-carboxylate (CE8 from BDH) and 4-n-dodecyloxy biphenyl-4'-(2'-methylbutyl) benzoate (C12) in the vicinity of the virtual cholesteric-smectic A-smectic C* (Ch-A-C*) point. The study revealed that the twist grain boundary (TGB) phase intervenes between the Ch and A phases in accordance with the prediction of the Renn and

Lubensky model[2,3]. The TGB phase was identified by the characteristic filament texture, also called vermis texture (Figure 1) and confirmed by X-ray and selective reflection studies.

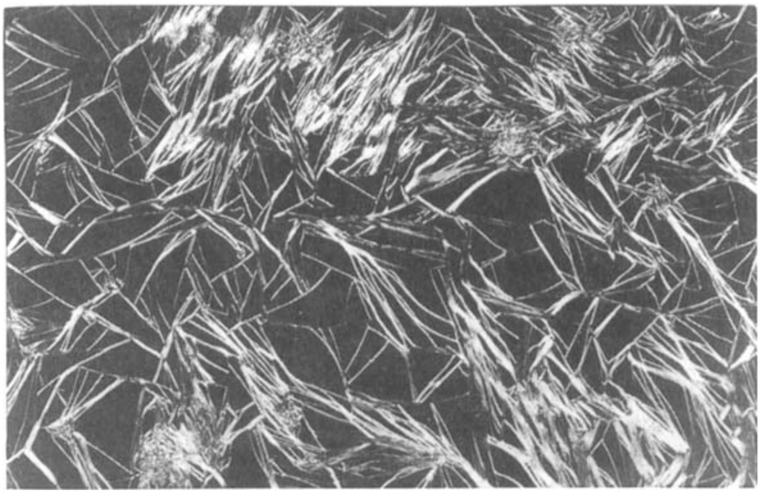

Figure 1: The filament texture characteristic of the TGB phase as seen when the sample is cooled from the Ch phase. (Magnification:X=125)

In the present paper, we report high pressure measurements on this binary system for different concentrations and discuss the nature of the nature phase diagrams obtained.

EXPERIMENTAL

The temperature-concentration (T-X) phase diagram for the binary system obtained at room pressure is shown in Figure 2. Pressure studies were carried out on this system for three concentrations, X=0.64, X=0.61 and X=0.25 (where X is the weight fraction of C12), indicated by arrows in Figure 2. The pressure-temperature (P-T) diagram for each value of X was mapped using a hydrostatic high pressure system in which the sample is enclosed between two sapphire rods and the transition detected by the laser transmission technique. Details of the apparatus and the experimental procedure have been described in detail in an earlier paper[4].

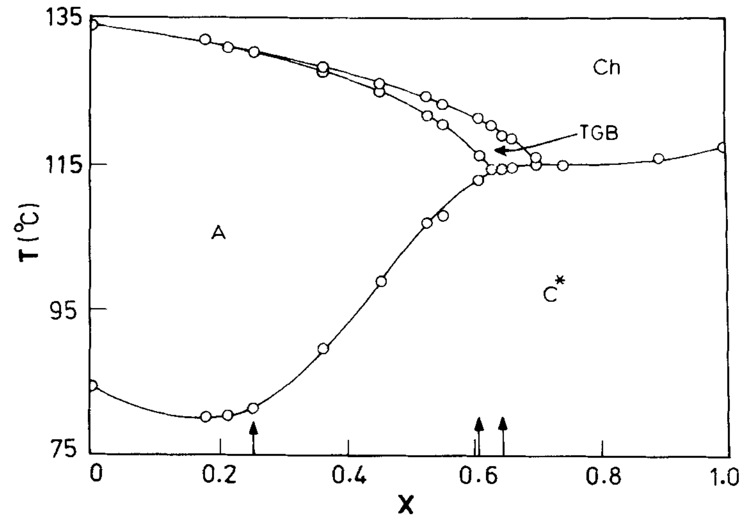

Figure 2: Partial temperature-concentration (T-X) diagram for CE8/C12 binary system at room pressure. X is the weight fraction of C12 in the mixture. The solid lines are meant to serve as a guide to the eye. The vertical arrows indicate the concentrations (X=0.25, 0.61 and 0.64) at which the pressure studies have been carried out.

RESULTS AND DISCUSSION

The P-T phase diagram for X=0.61 is presented in Figure 3. At 1 bar the Ch-TGB, TGB-A and A-C* transition temperatures are 121.5°C, 116.7°C and 113.2°C respectively, and with increasing pressure the range of the TGB phase increases very slightly, while the range of the A phase increases appreciably. The slopes of the Ch-TGB, TGB-A and A-C* transition lines, determined by least-square fits, are 35.4°C-kbar, 35.2°C/kbar and 27.5°C/kbar respectively.

It is worth pointing out that the above behaviour of the TGB phase under pressure is different from that exhibited by 1-methyl heptyl 4'-[[(4''-tetradecyloxy phenyl) propioloyl]-oxy] biphenyl-4-carboxylate (14P1M7) which shows the following sequence of transitions at 1 bar: isotropic-TGB-C*. In the latter case the TGB phase gets bounded on application of pressure[5].

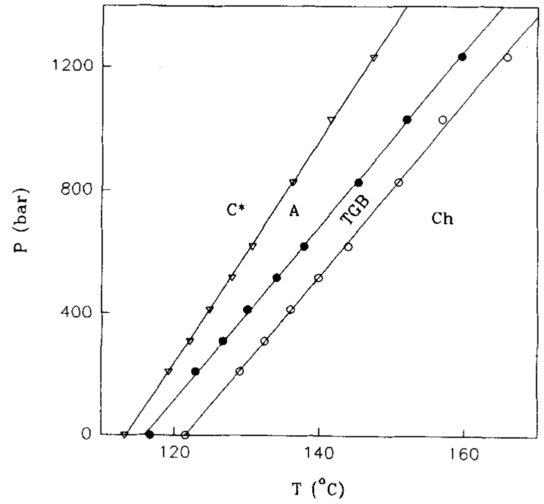

Figure 3: Global pressure-temperature (P-T) phase diagram for X=0.61

PRESSURE INDUCED TGB PHASE

The P-T diagram for X=0.25 is shown in Figure 4. Up to about 460 bar the Ch phase transforms directly to the A phase. Above this pressure, a new intermediate phase appears between the Ch and A phases. In order to identify this phase we made optical microscopic observations using a long-focus polarising stereo microscope (Wild M-42). While the phase diagram was obtained by using both the homeotropic and planar alignment geometries, visual observations were made using the homeotropic geometry. The A phase now appears pseudo isotropic, the field of view being dark between crossed polars. On heating the A phase, the intermediate phase shows up by the appearance of the filament or vermis texture, characteristic of the TGB phase identical to that shown in Figure 1.

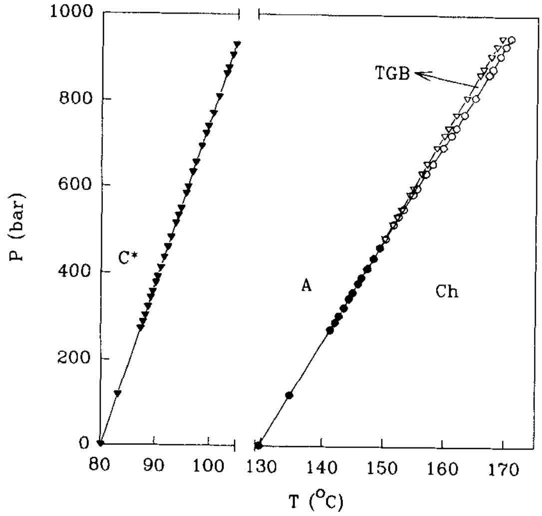

Figure 4: Global P-T diagram for X=0.25

As seen from Figure 4, the temperature range of the pressure induced TGB phase increases very slowly with pressure. This feature, along with the fact that the slopes of the phase boundaries are quite large, make the analysis of the topology of the phase diagram near the Ch-TGB-A meeting point rather difficult. In order to overcome this problem, the (P,T) data for the Ch-A boundary was fitted to a straight line and the raw data for all the three phase boundaries was normalised by subtracting out the slope obtained from the fit. (The slopes for Ch-A and Ch-TGB lines near the meeting point are the same, viz., 42.9°C/kbar. For the A-C* line the slope is 26.4°C/kbar). Figure 5 shows a plot of the reduced temperature versus pressure obtained in this fashion, revealing the topology quite clearly.

Two striking features of the phase diagram near the Ch-TGB-A meeting point are i) the Ch-A and Ch-TGB lines are collinear and ii) the TGB-A line intersects at an angle. The collinearity of the Ch-A and Ch-TGB lines (within experimental limits) was confirmed by fitting the data close to the meeting point. These topological features are characteristic as a critical end point (CEP), where as the theory of

Lubensky and Renn[2] predicts a bicritical point for the meeting of the Ch, TGB and A phases. One reason for the disagreement could be that the theoretical analysis is a mean field one and fluctuations may be playing a dominant role. In fact, the present topology is similar to the CEP topology observed[6] in a frustrated smectic system (smectic A_d-reentrant nematic-smectic A_1) for which again the mean field theory[7] predicts a bicritical point. In the latter case it was suggested that perhaps the expected bicritical point splits into the observed CEP-tricritical point combination. Borrowing the analogy it is possible that perhaps the Ch-TGB transition is first order close to the meeting point and changes over to second order, through a tricritical point, away from the meeting point.

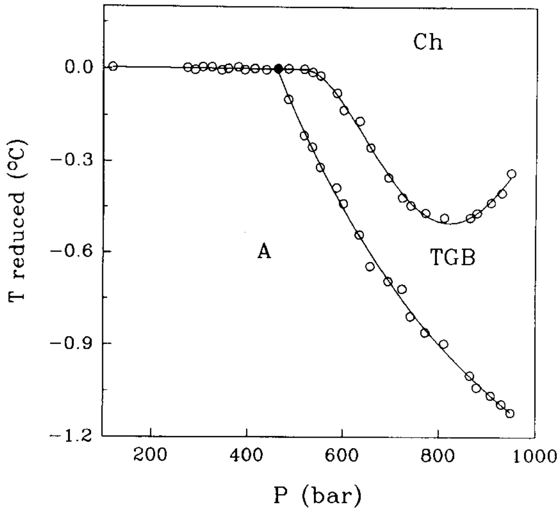

Figure 5: Reduced pressure versus temperature diagram in the vicinity of the Ch-TGB-A meeting point. The meeting point is indicated by a solid circle.

The present phase diagram as well as an earlier observation of a pressure induced NAC point[8] seem to suggest that pressure has the effect of making $C_\perp$, the coefficient of the gradient term in the Chen-Lubensky free energy more negative. Further experiments are needed to confirm this.

PRESSURE INDUCED SMECTIC A PHASE

From Figure 3 we note that the extrapolation of the A-C* and TGB-A lines to negative pressure leads to a virtual TGB-A-C* meeting point. This suggests[9] the possibility of observing a pressure induced A phase between the TGB and C* phases in a material for which the transition sequence as Ch-TGB-C*. To test this idea experiments were conducted on the binary system for X=0.64. Figure 6 shows the P-T diagram and as can be seen there is indeed a pressure induced A phase between the TGB and C* phase. The A phase was identified by optical microscopic observations as described earlier. A similar result has been reported by Anakkar et al[10] in another system. The slopes for the TGB-A, TGB-C* and A-C* near the meeting point, determined by least square fits, are 48°C/kbar, 23°C/kbar and 28°C/kbar respectively. The slope for the Ch-TGB line is 32.4°C/kbar. The topology of the phase diagram suggest that the TGB-A-C* meeting point is a bicritical point. We propose to conduct further studies with a view to establishing this point.

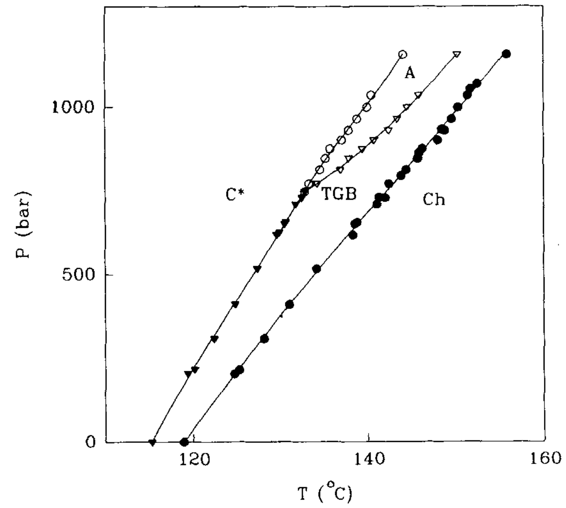

Figure 6: P-T diagram for X=0.64

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