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Experimental observation of multicritical points with TGB phases on a pure compound

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High pressure studies for the $n = 12$ homologues of the 3-fluoro-4((R) or (S)-methylheptyloxy)-4′-(4-alkyloxy-3-fluorobenzoyloxy) tolanes series have been performed by thermobarometric analysis. The phase sequence presents two Twist Grain Boundary phases denoted TGB_A and TGB_C. The pressure–temperature phase diagram has been determined; it exhibits a S_C^* phase, and an induced phase identified as S_A which does not exist under atmospheric pressure. The TGB_A temperature stability domain versus pressure first increases, then rises to a maximum and finally disappears. Such phase behaviour leads to an experimental observation of two multicritical points S_C^*–S_A–TGB_A and S_A–TGB_A–N^* for the pure compound under high pressures. This result confirms the existence of singular points previously predicted by the Renn–Lubensky theory.

1. Introduction

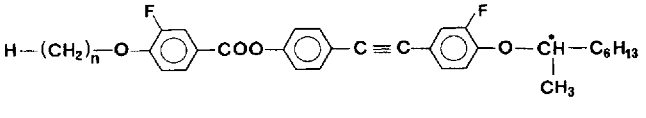
Numerous publications have shown that liquid crystals are materials especially well-fitted to theoretical and experimental studies of critical phenomena. Although the evidence of such thermodynamic behaviour is most often improved on magnetic field–temperature (*H–T*) and temperature–concentration (*T–X*) phase diagrams [1, 2], it is rarely shown on pressure–temperature phase diagrams, especially for multicritical points.

For liquid crystals, however, multicritical points of the Nematic–Smectic A–Smectic C (NAC point for short) type for achiral molecules [3, 4] and Cholesteric–Smectic A–twisted Smectic C type (N*AC*) for chiral molecules [5] have been observed on pressure–temperature (*P–T*) phase diagrams. In 1992, Renn and Lubensky [6–9] calculated three phase diagrams exhibiting the new Twist Grain Boundary (TGB) smectic phases in which several multicritical points were displayed. Up to now, five multicritical points S_C^*–S_A–TGB_A [9], S_A–TGB_A–N^* [10], S_C^*–TGB_C–N^* [11, 12], S_C^*–TGB_C–TGB_A [11] and N^*–TGB_A–TGB_C [11] have been observed for binary mixtures of ferroelectric liquid crystal (FLC) materials on temperature–concentration or pressure–temperature phase diagrams. However, among these different multicritical points, only the S_C^*–S_A–TGB_A type has been observed on a pressure–temperature phase diagram for a single component [13].

In order to give experimental evidence of new multicritical points on a pure FLC compound, we report here thermobarometric and calorimetric measurements performed on a compound for which a TGB_A phase, and recently a TGB_C phase, have been observed. This work is part of a more general study of the effect of pressure on phase sequences, on thermal stability of phases and on order of transition for new FLC compounds involving TGB phases.

2. Compounds

Our present studies relate to a homologous series of chiral molecules: the 3-fluoro-4((R) or (S)-methylheptyloxy)-4′-(4-alkyloxy-3-fluorobenzoyloxy) tolanes (abbreviated to nFBTFO$_1$M$_7$) [14]:



Phase identifications and transition temperatures have been determined by both thermal microscopy and differential scanning calorimetry [14]. This homologous

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series is very interesting for several reasons. It exhibits TGB_A phases for all the synthesized homologues. Moreover, we have just identified a TGB_C phase for the $n = 12$, 13 and 14 homologues by thermomicroscopic method of helix pitch measurements [15]. Usually, for chemical series, systematic variation of aliphatic chain lengths considerably influences the thermal stability for all phases. Similarly, the few experimental studies that have been carried out under high pressure show that some phases can appear or disappear as a function of pressure. In both cases, such behaviour leads to triple and/or multicritical points on phase diagrams. Thus, for example, for FLC materials in binary mixture, a N^*–TGB_C–S_C^* multicritical point [12] has been observed under pressure. Then, pressure studies on pure homologues of the nFBTFO$_1$M$_7$ series made it possible to predict the original phase behaviour. In fact, P–T phase diagrams for homologues with $n = 10$, 11, 16 and 18 have been established [13, 16] and give evidence of a TGB_A–N^*–I triple point [16] and a S_C^*–S_A–TGB_A multicritical point [13]. Previous measurements for the $n = 12$ homologue appeared unsatisfactory however; results are now properly established and they are original. We present here only pressure measurements.

According to microscopic and thermal analysis, the $n = 12$ homologue exhibits the following phase sequence:

Cr 69°C S_C^* 98·6°C TGB_C 98·9°C TGB_A
99·9°C N* 102·7°C BP 103·7°C I

Cr is a crystalline phase, BP a blue phase and I the isotropic phase. The TGB_C phase has been identified lying between S_C^* and TGB_A by optical studies of helical pitch versus temperature, under atmospheric pressure [15]. This phase had not been detected in our first experiments and is not mentioned in our first publication [14]; accurate measurements show that the thermal stability domain is less than 0·3°C when observed on cooling, and does not exceed 0·1°C on heating; details of our results for the helical pitch measurements are published separately [15].

3. Method

Studies of phase transitions have been performed under pressure by thermobarometric analysis (TBA) using an automated metabolemeter (SCERES, MAB 02 A 20). Measurements consist of recording, versus temperature, the pressure of a small sample (about 10 mg) enclosed in a metallic cell. Details of the method and the interpretation and exploitation of thermobarograms are given elsewhere [17–20]. Measurements have been performed for temperatures between 30 and 160°C and for pressures up to 1600 bars. Thermobarograms are plotted for a 0·5°C min^{-1} heating rate.

Complementary phase sequence studies were carried out under atmospheric pressure by differential scanning calorimetry (Seiko Instrument DSC 220 C). The thermograms are plotted for 0·5°C min^{-1} heating and cooling rates.

4. Results and discussion

Figure 1 gives a DSC scan obtained on cooling and shows a small shoulder on the peak that appears at 98°C. Such behaviour has already been observed for another series [11]. This confirms the existence of the TGB_C phase that has been found by optical measurements. However, on heating, the shoulder cannot be resolved on thermograms because of the narrowness of the thermal range of the TGB_C phase (see for example figure 4 in [14]).

Exploitation of thermobarogram networks, including several heating runs plotted for different initial conditions, lead to the pressure–temperature phase diagram presented in figure 2. Full lines and dashed lines correspond, respectively, to first order phase transitions and weakly first order or second order phase transitions. The pressure–temperature domains of Cr, S_C^*, TGB_A, N*, BP and I are identified from phase sequences determined under atmospheric pressure [14]. Thermobarograms plotted for pressures near atmospheric pressure did not allow us to determine a P–T domain for the TGB_C phase; in fact, the thermal stability range determined by optical measurements under atmospheric pressure is less than 0·1°C, and is too small to be separated using the present P–T equipment.

The phase diagram is interesting for several reasons. First of all, for the first time by thermobarometric measurement, the pressure and temperature ranges of

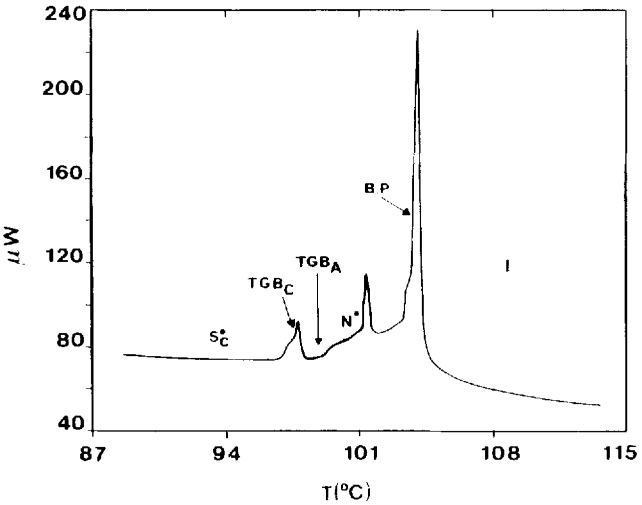

Figure 1. Differential scanning calorimetry thermogram for the cooling cycle of 12FBTFO$_1$M$_7$.

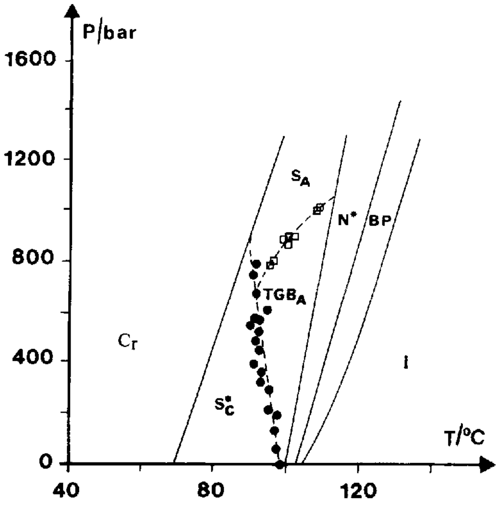

Figure 2. Pressure–temperature phase diagram for $12FBTFO_1M_7$; full lines: first order phase transitions; dashed lines: weakly first order or second order phase transitions.

stability of a Blue Phase have been separated from the N* phase; both stability domains of BP and N* regularly increase with pressure and temperature. Under pressure, the behaviour of the TGB_A phase is unexpected; at first, the temperature stability domain increases with a decrease for the S_C^* phase, rises to a maximum, and finally decreases and disappears for higher pressures. Therefore, the *P–T* diagram shows two pressure bounded mesophases, a S_C^* and a TGB_A phase and a pressure induced phase that leads to three singular points. The induced phase appears between S_C^* and TGB_A and might be identified as TGB_C; in this case, the *P–T* domain for the TGB_C phase would stay very narrow until 645 bars, and would suddenly become very large for higher pressure. Moreover, the transition between the induced phase and N* is observed to be second order; the transition between the induced phase and TGB_A is detected as first order near 900 bars. These circumstances do not favour a TGB_C phase; in fact, for the very few known examples, TGB_C–N* [21, 22] and TGB_C–TGB_A [15, 21] transitions are, respectively, first and second order. More reasonably (figure 2), taking into account first the phase sequence under atmospheric pressure [14] where, by increasing chain length, S_C^* appears with disappearance of S_A, and second the *P–T* phase diagram previously plotted for $n = 11$, where the pressure induces a S_A phase from about 130 bars [13], the induced phase for the present compound ($n = 12$) from about 675 bars can be identified as S_A; then, whatever the pressure, the thermal domain of TGB_C is always too small to be detected and/or can disappear on increasing the pressure.

On thermobarograms, melting transitions (Cr–S_C^* and Cr–S_A) are always found as first order. The TGB_A–N* transition is detected as weakly first order (pressure jump lower than 15 bars) for lower pressures and becomes second order (disappearance of pressure increments) near the singular point; the S_A–N* transformation is always observed as second order. Along the S_A–TGB_A boundary line, the transition is detected as weakly first order near 900 bars and as second order for other pressures. Lastly, both S_C^*–TGB_A and S_C^*–S_A transitions are always observed as second order. It must be noted here that the slopes of the S_C^*–TGB_A and S_C^*–S_A phase transitions are negative. A discussion of this unexpected phenomenon is proposed here. First order transitions are characterized by a discontinuous change of volume (ΔV) and a latent heat (ΔH). They satisfy the following Clausius–Clapeyron equation [23]:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)^{\mathrm{Tr}} = \frac{\Delta H}{T\Delta V}. \tag{1}$$

Thus, by heating, the negative slope implies that the volume variation at the transition is negative. This behaviour is given by water, bismuth, germanium and thallium. However, to our knowledge, no experimental evidence of such behaviour has been produced for liquid crystals [24]; therefore, it appears that negative slopes on the phase diagram are probably connected with the second order nature of the transitions. This is confirmed by our present measurements on the S_C^*–S_A and S_C^*–TGB_A transitions; if no experimental data are known, therefore, it is not reasonable to class systematically as first order all transitions with negative slopes on *P–T* diagrams [25]. For second order transitions, the volume and entropy remain constant, but there are discontinuities for the compressibility χ, the thermal expansion α and specific heat C_p. When discontinuities of thermodynamic coefficients have finite values, the slopes of *P–T* diagrams are given by the following Ehrenfest (or Keesom) relation [26]:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)^{\mathrm{Tr}} = \frac{\Delta\alpha}{\Delta\chi} = \frac{\Delta C_p}{TV\Delta\alpha}. \tag{2}$$

Theory and experimental specific heat measurements [1–2] show that specific heat changes at transitions are never positive with increasing temperature. Such cases are presented by the conductor–superconductor transition, the transition from normal liquid to superfluid state, and S_C–S_A [1] and S_C–N [1] transitions for liquid crystals. When slopes are negative, the transformations correspond to α and χ variations which are, respectively, positive and negative.

Because melting transitions are always first order transformations, Cr–S_C^*–S_A (90 ± 5°C, 900 ± 60 bars) is necessarily a triple point; then, the S_C^*–S_A transition must become first order on approaching the melting

Table. Experimental data for the phases and transitions for $12FBTFO_1M_7$.

	Cr		S_C^*		TGB_C	S_A	TGB_A		N*		BP		I
$T^{(1)}$	●	69	●	98·6	—	—	●	99·9	●	102·7	●	103.7	●
$T^{(2)}$	●	68·5	●	98·6	●	—	●	101·5	●	103·9	●	104·6	●
$\Delta H^{(1)}$	●	23·6	●	0·15	—		●	0·12	●		●	3·10*	●
$\Delta H^{(2)}$	●	28·6	●	0·19*	●		●	0·13	●		●	1·96*	●
$\left(\frac{dP}{dT}\right)^{Tr}$	●	44·2	●	−106·0	—		●	87·1	●	53·1	●	23·9	●
$\left(\frac{dP}{dT}\right)_V$			10·5			$11·9^+$	11·0		12·2		13·7		
$\Delta V_{Tr}^{(1)}$		15·6						0·037				$3·44^{\otimes}$	
$\Delta V_{Tr}^{(2)}$		18·9						0·039				$2.17^{\otimes}$	

T: transition temperature (°C) under atmospheric pressure; ⁽¹⁾by Perkin-Elmer D.S.C 7 [14], ⁽²⁾by Seiko Instruments D.S.C. 220C and thermomicroscopic analysis.

ΔH: transition enthalpies (kJ mol^{-1}) under atmospheric pressure; ⁽¹⁾by Perkin-Elmer D.S.C. 7, ⁽²⁾By Seiko Instrument D.S.C. 220C.

● means the phase exists for the compound; — means the phase does not exist for the compound; + under pressure: *the sum of two transitions N*–BP and BP–I or S_C^*–TGB_C and TGB_C–TGB_A.

$\left(\frac{dP}{dT}\right)^{Tr}$: slope of boundary lines (bars K^{-1}) of the *P–T* phase diagram; $\left(\frac{dP}{dT}\right)_V = \frac{\alpha}{\chi}$: slope of thermobarograms out of the transitions (bars K^{-1}).

ΔV: volume change (cm^3 mol^{-1}) at transitions calculated by Clausius–Clapeyron equation; ⊗ volume change of N*–I transition, including the BP phase.

curve. Following the preceding discussion, the slope of the S_C^*–S_A boundary line should be positive. At the neighbouring of S_C^*–S_A–TGB_A (91·5 ± 5°C, 675 ± 20 bars) and S_A–TGB_A–N* (113 ± 5°C, 1060 ± 20 bars) points, all transitions are second order; both points are necessarily multicritical, and correspond respectively, to the B_1 and B_2 points on Renn–Lubensky diagrams [9]. Data for each boundary line of the compound are reported in the table.

5. Conclusion

Thermobarometric measurements have been performed on the $n = 12$ homologue of the nFBTFO$_1$M$_7$ chiral chemical series. The pressure–temperature phase diagram shows an induced phase which can be identified as S_A; also, evidence of a Cr–S_C^*–S_A triple point and of S_C^*–S_A–TGB_A and S_A–TGB_A–N* multicritical points is given under high pressure. This result is in good agreement with the Renn–Lubensky theory. The negative slope for the S_C^*–TGB_A and S_C^*–S_A transition is probably related to the second order nature of both transitions. This work corresponds to the first observation of a S_A–TGB_A–N* multicritical point under pressure for a single component system.

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