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FIRST OBSERVATION OF A S^*_C–S_A–TGB$_A$ MULTICRITICAL POINT IN A PURE COMPOUND

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Abstract

High pressure experiments have been performed by thermobarometric analysis on two homologous (n = 10 and 11) of the [3-fluoro-4((*R*) or (*S*)-methylheptyloxy) 4′–(4″–alkoxy-3″-fluorobenzoyloxy) tolans series, which both exhibit the TΓB$_A$ phase. The character (first or/and second order) of the transitions involving the TGB$_A$ phase are determined from thermobarograms. The pressure–temperature phase diagrams show that the TGB$_A$ phase is stabilized under high pressure for the two compounds. For n = 11 an induced S_A phase is observed under high pressures leading to the first experimental observation, on pressure–temperature phase diagram of pure compounds, of a S^*_C–S_A–TGB$_A$ multicritical point, previously predicted by the Renn-Lubensky theory.

Keywords: thermobarometric analysis

Introduction

For liquid crystals, the chirality of the molecules induces an helicoidal structure for the mesophases. Then, between the crystalline (*K*) and the isotropic liquid (*I*), it can be observed, *vs.* temperature, mesophases with a twist perpendicular to the molecules (as in the cholesteric phase: N^*) or perpendicular to the layers forming the liquid crystalline structure – but, only when the molecules are tilted in the layers-(as in the twisted smectic *C* phase S^*_C). Twist grain boundary (TGB) structures have also been predicted [1] for mesophases corresponding to a twist of smectic blocs along an axis parallel to the layers; in these structures, the molecules can be perpendicular to the smectic layers (as in the TGB$_A$ phase) as well as tilted in the layers (as in the TGB$^*_C$ with S^*_C smectic

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blocs or as in the TGB$_C$ with S_C un-twisted smectic blocs). Recently, the TGB$_A$ and TGB$_C$ phases have been observed experimentally [2–4].

In 1988, Renn and Lubensky [1], then, more recently Renn [5] have suggested that the TGB structures could appear – for certain chiral compounds – near a (NAC)* multicritical point. Introducing a term of energy – due to the chirality – in the elastic energy of the molecules, and minimizing the free energy, Renn has calculated three phase diagrams exhibiting the new TGB phases, according to the relative values of the bend, splay and twist elastic constants. Figure 1 reproduces the theoretical phase diagram when the splay and twist constants are lower than the bend rigidity; the phase domains are represented in a (r, $c_\perp$) diagram, where r and $c_\perp$ are Gibbs energy parameters which can be temperature and pressure functions. The (NAC)* point partitions into several multicritical points B_i for which occurs TGB phases. Up to date, the S_C^*–S_A–TGB$_A$ [5], S_A–TGB$_A$–N^* [6], S_C^*–TGB$_C$–N^* [4] and S_C^*–TGB$_C$–TGB$_A$ [4] points have been observed, but only for binary mixtures on temperature–concentration phase diagrams. However, such points have never been observed for single component on pressure–temperature diagrams. Then, we have carried out thermobarometric analysis on new chiral compounds exhibiting TGB$_A$ phases in order to put in evidence, on P–T phase diagrams, one of the multicritical points predicted by Renn (Fig. 1) and to study the effect of pressure on the stability domains of the TGB$_A$ phase. In fact, this paper corresponds to the first high pressure study of ferroelectric liquid crystals exhibiting TGB phases.

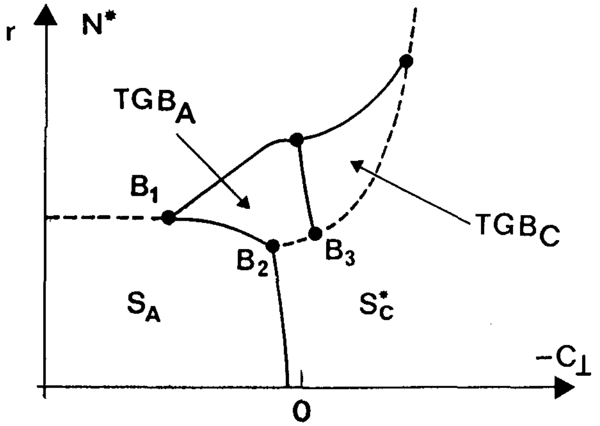
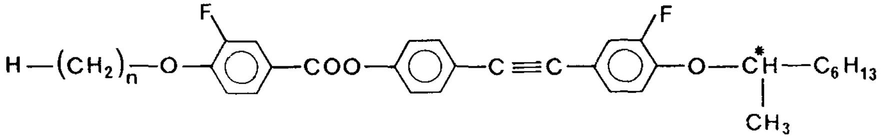


Fig. 1 Theoretical phase diagram predicted by Renn when the splay and twist constants are lower than the bend rigidity (reproduced from reference [5])

Compounds

The choice has been taken on the homologous series with chiral molecules: [3-fluoro-4((*R*) or (*S*)-methylheptyloxy)4′-(4″-alkoxy-3″-fluorobenzoyloxy) tolans] (shortly: nFBTFO$_1$M$_7$) which has been synthesized by Nguyen *et al.* [3] and which chemical formula is:



This series exhibits a rich polymorphism. Especially, it is the one that shows the S_A S_C^* and TGB$_A$ phases simultaneously. The TGB$_A$ phase exists for all the synthesized homologous but on a very narrow domain of temperature (less than 3°C). Phase sequences *vs.* alkoxy chain length show that the S_A phase domain (for 7 to 10) decreases on behalf of the S_C^* phase (from 41.4°C for $n = 9$ to 8.4°C for $n = 10$) and of the TGB$_A$ phase, then vanishes for $n = 11$; the phase sequences are K–S_A–TGB$_A$–N^*–I for $n = 7$, 8 and 9, K–S_C^*–S_A–TGB$_A$–N^*–I for $n = 10$ and K–S_C^*–TGB$_A$–N^*–I for $n = 11$.

Calorimetric measurements have been performed by Bouchta *et al.* [3] using a Perkin Elmer DSC-7. DSC curves show a change of appearance for the S_A–TGB$_A$ transition by increasing n from 7 to 11; in fact this transition is weakly first order for $n = 7$, 8 and 9, and becomes practically second order for $n = 10$. These behaviours let predict that some homologous could exhibit multicritical phenomena under pressure. To try to put in evidence such phenomena, we have studied the compound with $n = 11$; in fact, by analogy with polar compounds showing reentrant phases [7–9], this homologous is apt to present a S_A phase induced with pressure. On another hand, to study the changes, *vs.* pressure, of the phase sequences including TGB$_A$ phases, the compound with $n = 10$ was also investigated.

Method

The phase transitions of both compounds have been studied under pressure by thermobarometric analysis (TBA) using an automated metabolemeter (M.T.M. leader, MAB 02A20). Measurements consist to record, *vs.* temperature, the pressure of a sample enclosed in a metallic cell [10]. Details relating to the method, interpretations and exploitations of thermobarograms $[P=f(T)]$v are given elsewhere [11–13].

The main advantages of TBA for liquid crystals investigations is i) to allow the detection of transitions which are observable by other methods with difficulties (weakly first order or second order transitions) ii) to be efficient on small samples.

In our experiments, the temperature range is 30 to 160°C, and the pressure range is 0 to 1 kbar. The amount of compound is about 10 mg. Thermobarograms are plotted by heating with a 0.5 deg·min^{-1} rate.

Results

Examples of thermobarograms obtained for n = 10 and n = 11 are reported on Figs 2a–c and 3a–e respectively. For both compounds, the melting (K–S_C^* transition) is detected by an abrupt pressure increment (Figs 2a and 3a); the slopes of the equilibrium curve are about 40 and 33 bars K^{-1} and are in good agreement with literature data for first order phase transitions [11, 12]. The upper part of the thermobarograms corresponds to the pressure increase, *vs*. temperature, of the S_C^* phase. At low temperature, only a basic line is recorded, that corresponds to the expansion (in crystalline phase) of the compound when filling up the free volume comprised between the sample and the cover. Clarifica-

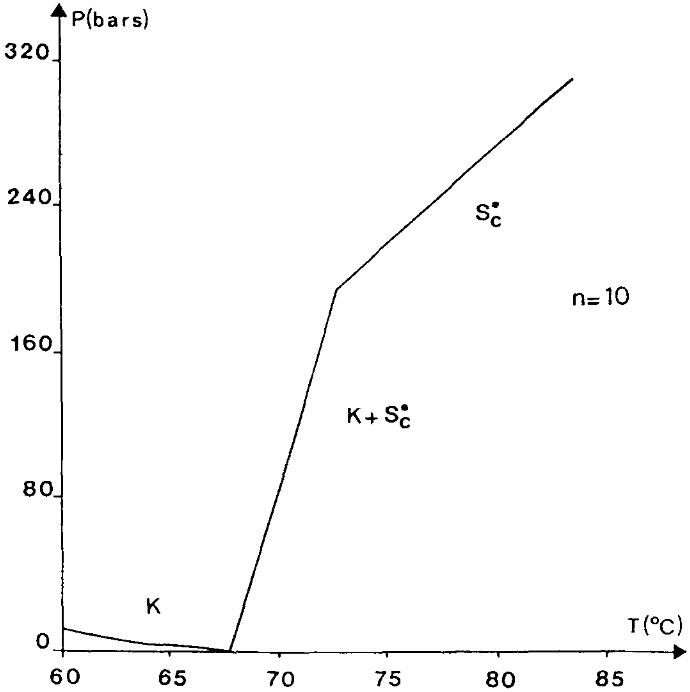


Fig. 2a Examples of thermobarograms obtained for $10FBTFO_1M_7$ showing: the melting polymorphism

tions (N^*–I transitions) are clearly detected (Figs 2b and c, 3b–e) as first order phase transitions.

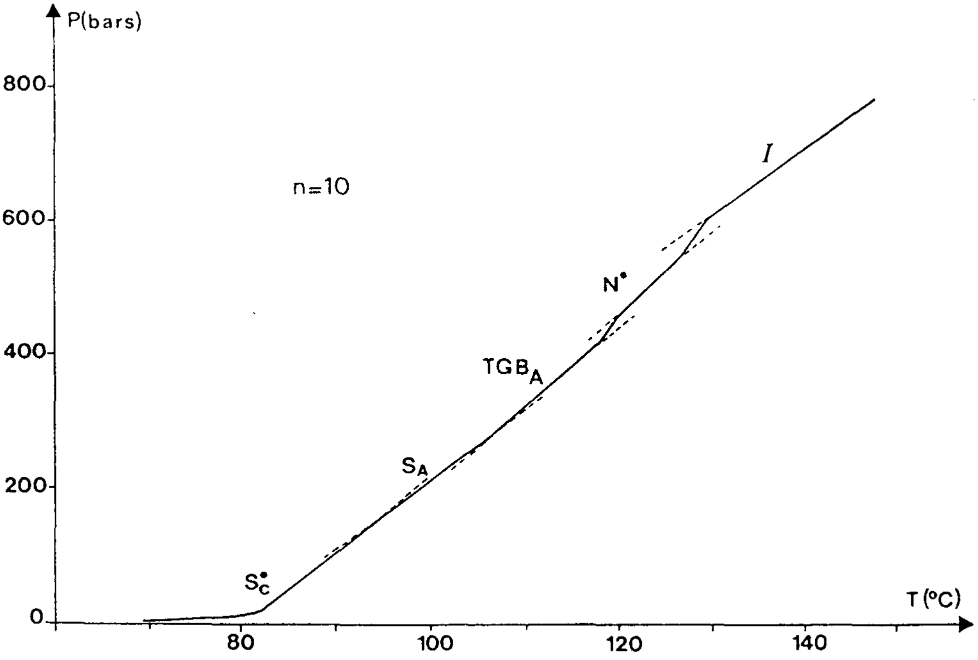


Fig. 2b Examples of thermobarograms obtained for $10FBTFO_1M_7$ showing the mesomorphic polymorphism

For $n = 10$, each phase existing under atmospheric pressure is also observed under high pressure (Figs 2b–c). The TGB_A–N^* transition is always detected as first order one. The S_C^*–S_A transition is clearly second order (no pressure increment). The S_A–TGB_A transformation is practically second order or weakly first order (existence of a small pressure change nearby experimental errors). Networks of thermobarograms lead to the pressure-temperature phase diagram (Fig. 4).

For $n = 11$ thermobarograms of Figs 3d–e exhibit at low temperature and pressure a small pressure change that is attributed to the end of the melting. Four stable phases can be observed under pressure on thermobarograms of Figs 3b and c, and the phase sequence is the same as under atmospheric pressure. Five stable phases are detected on Figs 3d and e where a pressure induced mesophase is observed. The resulting P–T phase diagram is presented (Fig. 5). Very recent optical observations under atmospheric pressure have shown the $n = 12$ to 14 exhibit a S_C^*–TGB_C–TGB_A–N^* sequence, with a TGB_C–TGB_A transformation which could be second order. However, thermobarograms (Figure 3d and e) show the transformation between the induced mesophase and the TGB$_A$ one is first order. Then, taking into account of i) the phase sequence under atmospheric pressure for 11FBTFO$_1$M$_7$ and ii) the phase sequence observed for 10FBTFO$_1$M$_7$. The induced mesophase is then a S_A phase; that allows the identifications of Figs 3d and e. Thus, the TGB$_A$–N^* transition is usually observed as first order (Figs 2c, d and e) but can also be practically second order (Fig. 2b). The S_C^*–TGB$_A$ transition is always second order. The two transitions S_C^*–S_A and S_A–TGB$_A$ bounded to the pressure induced S_A phase are respectively second order and weakly first order.

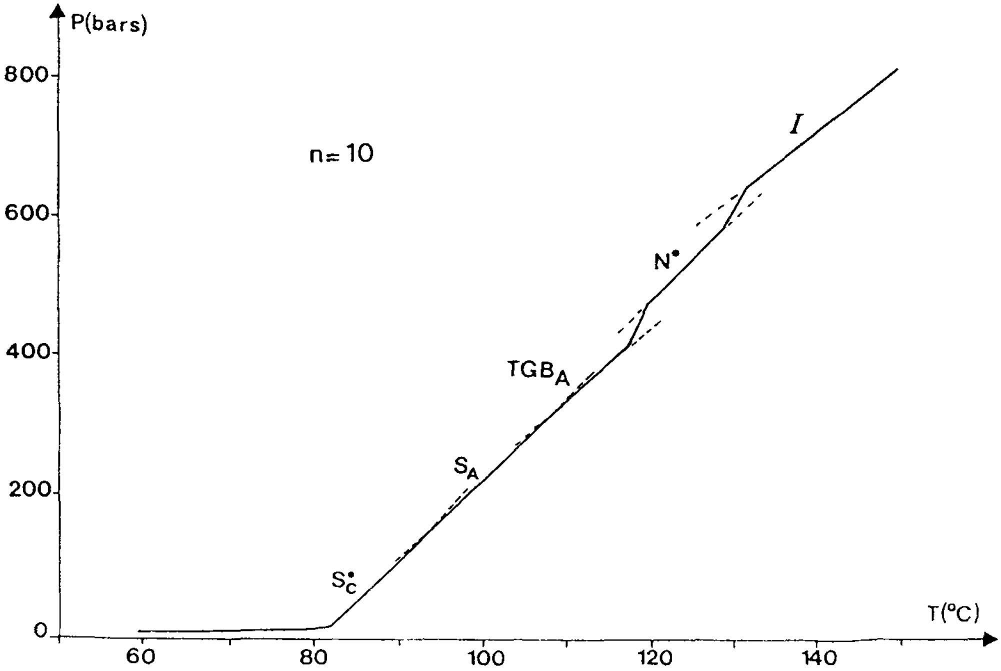


Fig. 2c Examples of thermobarograms obtained for 10FBTFO$_1$M$_7$ showing the mesomorphic polymorphism

Discussion

It is useful to note, there is a blue phase (*BP*) between the N^* and *I* phases. Under atmospheric pressure (thermomicroscopic measurements [3]) the *BP* phase exists on less than 0.2°C; it has not been observed by thermobarometric measurements.

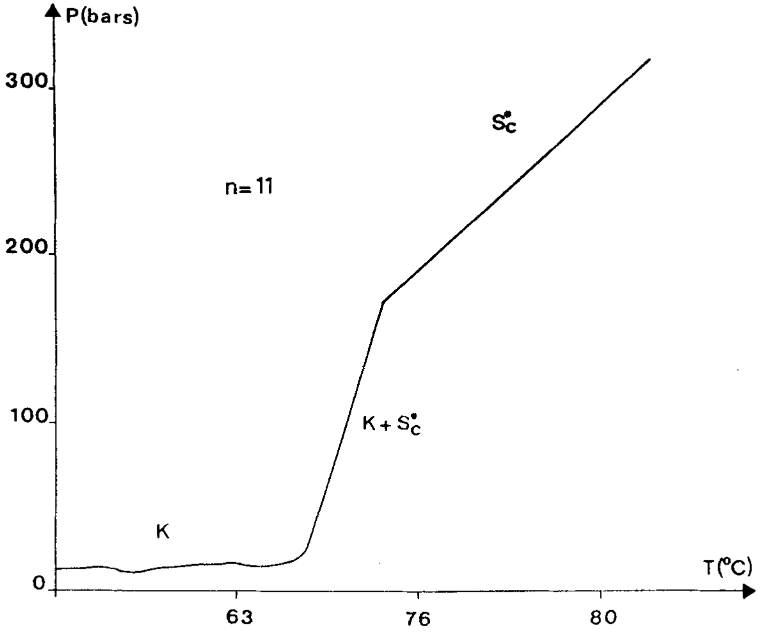


Fig. 3a Examples of thermobarograms obtained for 11FBTFO$_1$M$_7$ showing the melting polymorhism below the multicritical point

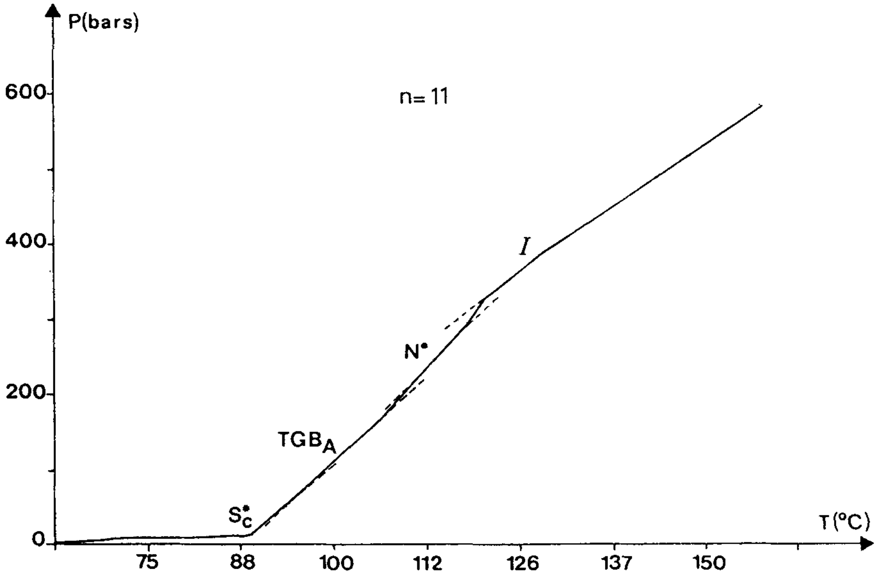


Fig. 3b Examples of thermobarograms obtained for 11FBTFO$_1$M$_7$ showing the mesomorphic polymorphism below the multicritical point

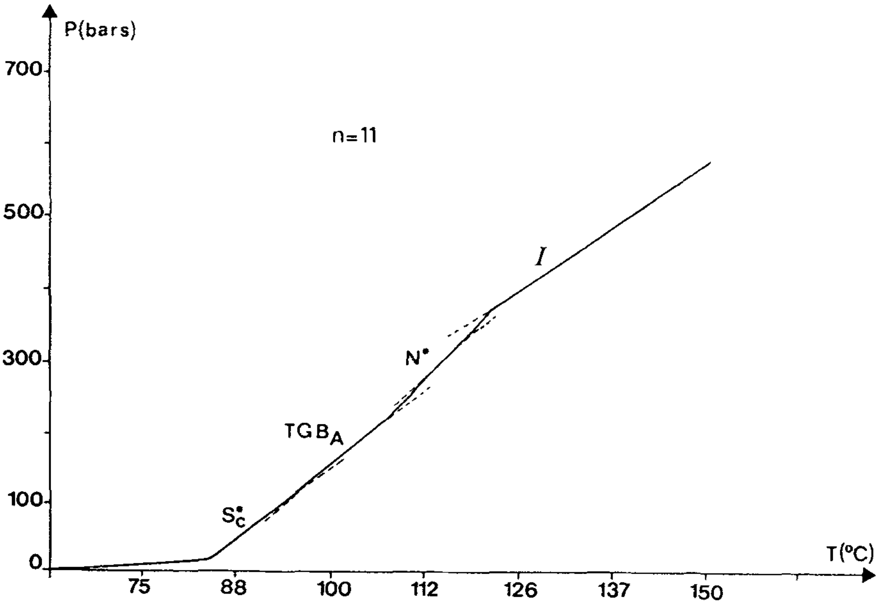


Fig. 3c Examples of thermobarograms obtained for 11FBTFO$_1$M$_7$ showing the mesomorphic polymorphism below the multicritical point

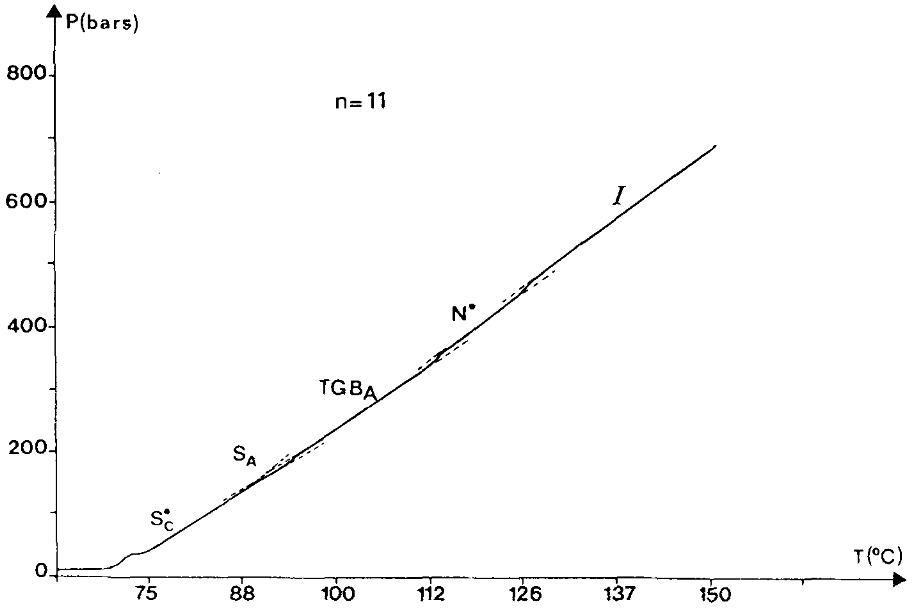


Fig. 3d Examples of thermobarograms obtained for 11FBTFO$_1$M$_7$ showing the mesomorphic polymorphism above the multicritical point

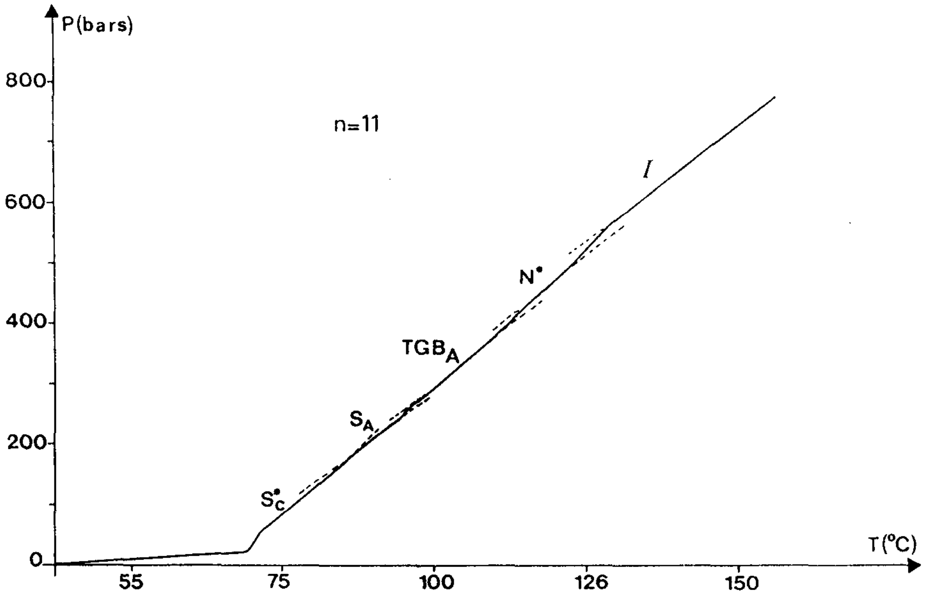


Fig. 3e Examples of thermobarograms obtained for $11FBTFO_1M_7$ showing the mesomorphic polymorphism above the multicritical point

For the phases, the ratio between the isobaric thermal expansion α and isothermal compressibility χ is given by the slopes of the thermobarograms out of the transition; data for each phase of both compounds are reported in Table 1.

On the *P–T* phase diagrams, transitions are reported as full lines for first order and dashed lines for second order. The slopes of the boundary lines are given by the Clapeyron relation:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)^{\mathrm{Tr}} = \frac{1}{T}\cdot\frac{\Delta H}{\Delta V} \qquad \text{for first order transitions [14]}$$

and by the Ehrenfest relation:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)^{\mathrm{Tr}} = \frac{\Delta\alpha}{\Delta\chi} \qquad \text{for the second order ones [15]}$$

data for each boundary line of both compounds are reported in Table 1.

The two *P–T* phase diagrams show that the domain of stability in temperature of the S_A, TGB_A and N^* phases increases with pressure even though it decreases with pressure for the S_C^* phase.

Table 1 Experimental data for the phases and transitions for the two homologous $n=10$ and $n=11$ of the [3-fluoro-4((R) or (S)-methylheptyloxy) 4'-(4''-alkoxy-3''-fluorobenzoyloxy)- tolans] series (shorthly $10FBTFO_1M_7$ and $11\ FBTFO_1M_7$)

Formula		K	S_C^*	S_A	TGB_A	N^*	I
$10FBTFO_1M_7$	T	• 67	• 92.8	• 102	• 103.5	• 106.5	•
	$(dP/dT)^{Tr}$	• 40	• –238	• 40	• 28.5	• 26.5	•
	$(dP/dT)_V$		10.2	9.9	11.3	12.3	9
$11FBTFO_1M_7$	T	• 68	• 97.5	–	• 101.5	• 106	•
	$(dP/dT)^{Tr}$	• 33	• –40	–	• 33.3	• 25	•
	$(dP/dT)^{Tr}$		• -12.5^+	• 50^+	•		
	$(dP/dT)_V$		7	7.1	7.2	8	7.1

T : Transition temperature (°C) under atmospheric pressure
$(dP/dT)^{Tr}$: Slope of boundary lines (bar K^{-1}) of the P–T phase diagram
$(dP/dT)_V$: Slope of thermobarograms out of the transitions (bar K^{-1})
K : Crystalline phase
S_C^* : Twisted smectic C phase
S_A : Smectic A phase
TGB_A : Twist grain boundary structure of the S_A phase
N^* : Cholesteric phase

• means the phase exists for the compound
– means the phase does not exist for the compound
+under pressure

For $n = 11$, the P–T phase diagram exhibits boundary lines: S_A–TGB_A (weakly first order) and S_A–S_C^*, S_C^*–TGB_A (second order) with a crossing point at $T = 94$°C and $P = 130$ bars: it is a S_C^*–S_A–TGB_A multicritical point (B_2 point in the Renn diagram Fig. 1). To our knowledge, it is the first observation of such multicritical point for pure compounds in the P–T plane. More, the appearance of a pressure induced S_A mesophase leads, by extrapolation, to the evidence of a virtual [S_A–TGB_A] transition at $T^{[S_A-TGB_A]} = 91.5$°C under atmo-spheric pressure; that transition could be observed by thermomicroscopy from cooling the TGB_A phase.

For $n = 10$, the extrapolation of the S_A–TGB_A and TGB_A–N^* boundary lines below atmospheric pressure, suggests a virtual S_A–TGB_A–N^* multicritical point (B_1 point in the Renn diagram). Such point could only be observed in metastable – or not stable-states for negative pressures using piezothermal measurements. In the same way, for $n = 11$, a virtual S_A–TGB_A–N^* multicritical point is obtained from the extrapolation of the S_C^*–TGB_A and TGB_A–N^* boundary lines. Such multicritical point is not predicted by Renn.

Thus, it can be noted that in the theoretical Renn diagram, the N^*–TGB$_A$ transition is predicted as second order. Our experiments prove this transition is not purely second order, but can also be (weakly) first order (Figs 3b and c).

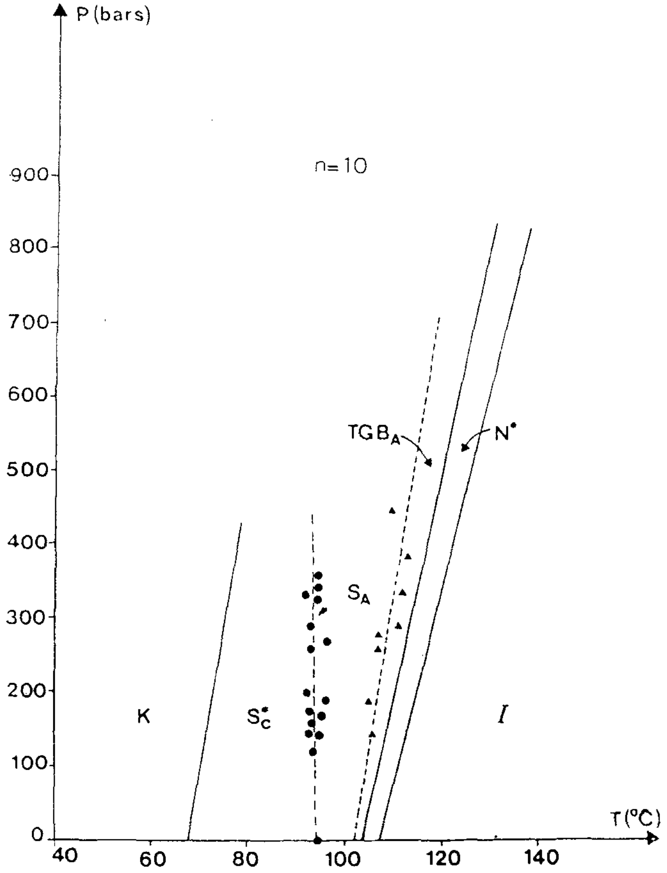


Fig. 4 Pressure–temperature phase diagram for 10FBTFO$_1$M$_7$: full lines: first order phase transitions; dashed lines: weakly first order or second order phase transitions

However, several causes affect the accuracy of our experiments. In fact, certain transitions are difficult to detect due to the smallness of the phase domains (TGB$_A$ phase domain for example). For weakly first order or second order transition, the detection is all the more critical that the ratios α/χ are close, for the two successive phase (S^*_C and TGB$_A$, S^*_C and S_A, S_A and TGB$_A$ for example). Consequently, the topology of the multicritical point S^*_C–S_A–TGB$_A$ cannot be stated without ambiguity; we need another method of analysis (under pressure) to improve this study. Especially, the piezothermal method [16–19], with his high sensitivity, will be used later on.

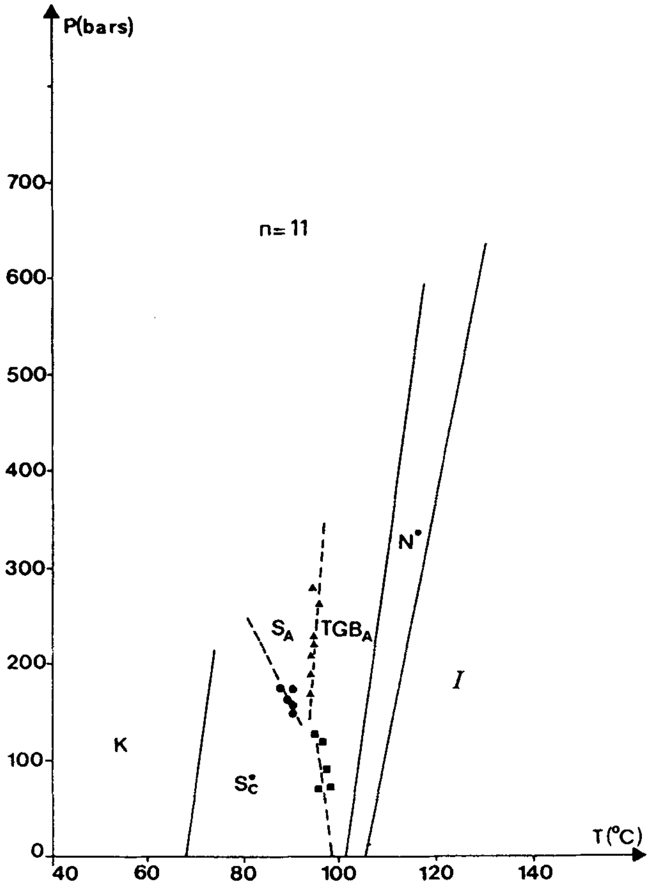


Fig. 5 Pressure –temperature phase diagram for 11FBTFO$_1$M$_7$: full lines: first order phase transitions; dashed lines: weakly first order or second order phase transitions

Conclusion

Thermobarometric measurements have been performed on two ferroelectric liquid crystals i.e. 10 and 11FBTFO$_1$M$_7$. It appears on thermobarograms that the TGB$_A$–N^* and N^*–I transitions are weakly first order, the S_A–TGB$_A$ transition is either first order or practically second order, the S_C^*–S_A and S_C^*–TGB$_A$ transitions are clearly second order. The pressure–temperature phase diagrams have been determined; for both compounds, the TGB$_A$ phase is stabilized under high pressure. For $11FBTFO_1M_7$, an induced S_A phase occurs in the P–T diagram leading to a S_C^*–S_A–TGB_A multicritical point. These studies are the first regarding the pressure effect on the TGB phases of ferroelectric liquid crystals and confirm part the Renn-Lubensky theory.

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Zusammenfassung — An zwei homologen (n =10 und 11) Reihen von [3-Fluoro-4((*R*) oder (*S*)-methylheptyloxy) 4′-(4″-alkoxy-3-fluorobenzoyloxy)-tolan, die beide eine TGB_A-Phase aufweisen, wurden durch thermobarometrische Analyse Hochdruckexperimente durchgeführt. Anhand der Thermobarogramme wurde der Charakter (erste oder/und zweite Ordnung) der mit der TGB_A-Phase verbundenen Übergänge ermittelt. Die Druck-Temperatur Phasendiagramme zeigen, daß die TGB_A-Phase unter hohem Druck bei beiden Verbindungen stabilisiert wird. Für $n=11$ wird unter hohem Druck eine S_A-Induktionsphase beobachtet, die bei Druck-Temperatur Phasendiagrammen von reinen Verbindungen zur ersten experimentellen Beobachtung eines multikritischen Punktes S_C^*-S_A-TGB_A führt, wie er zuvor von der Theorie von Renn-Lubensky prognostisiert wurde.