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Phase diagrams and phase transition studies of a homologous series with both tilted and orthogonal hexatic phases

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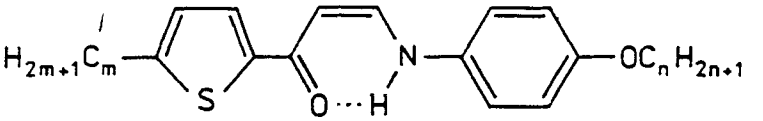
Both smectic hexatic phases, *Hex-B* and *Sm-F*, were found in some three-ring 2-methylthienyl derivatives terminated with alkoxyl substituents. In a homologous series THI, the molecular terminal chains promote either tilted (for short chains) or orthogonal (for long chains) hexatic mesophases. For intermediate length chains (having 14 or 15 carbon atoms), the phase sequence is *Hex-B - Sm-F - Sm-C - Sm-A*. This phase sequence allows observation of two new triple points involving *Hex-B* phase. For some halogen substituted thienyl derivatives other mixed-tilt type phase sequence, *Cry-G - Sm-F - Hex-B - Sm-A* is found. Phase transitions involving hexatic phases were studied by DSC and X-ray scattering method.

1. INTRODUCTION

Hexatic phases are examples of systems with short-range translational order, but long-range bond orientational order (BOO).[1,2] They have been predicted in 2D systems to exist as an intermediate state upon melting from crystal to liquid state. Liquid crystals are relatively rich in those phases but most of mesogenic materials exhibit tilted hexatic smectic phases, *Sm-F* and *Sm-I*. In contrary, the untilted hexatic smectic phase, *Hex-B*, has been so far encountered only in few compounds.[2] The thienyl derivatives presented in this paper are examples of compounds which exhibit transition between tilted and orthogonal hexatic

phases, *Hex-B* - *Sm-F*. Materials with transitions driven by molecular tilt, between phases with already established BOO, are of particular interest for testing theory of 2D melting, to examine the role of tilt-BOO coupling, as well as to study new multicritical points.[2]

We examined new group of enaminoketone compounds



hereafter abbreviated as mTHIn. Our preliminary studies showed that phase diagrams of homologous series are controlled by alkyl substituents of the thienyl ring. For m=0 only orthogonal phases, *Cry-B*, *Hex-B* and *Sm-A*, are observed and the corresponding series reveals typical generic phase diagram.[3] For m>2 present are only their tilted counterparts, *Cry-G*, *Sm-F* and *Sm-C*. For m=1 (THI series) both tilted and orthogonal smectic phases exist, and this interesting case is described in the paper.

2. RESULTS

2.1. Phase diagram and optical studies

The phase diagram of THI series (Figure 1) was established basing on optical and DSC methods. Under polarizing microscope all phases reveal typical textures[4] while studying free-suspended films as well as samples between surface-treated microscopic cover glasses. Homeotropic textures could be easily obtained for orthogonal phases (*Sm-A*, *Sm-B*); conoscopic observations confirm uniaxiality of these phases. Schlieren textures were observed for tilted phases, *Sm-C* and *Sm-F*, and the transition between them was characterized by intensive motions within the texture, followed by schlieren size changes. Patterns become more dark and schlieren texture finally vanishes to produce homeotropic orientation as the smectic-*B* phase is approached. Birefringence changes are gradual for THI15, but for lower homologues, sharp changes are well visible.

The phase diagram is, for short homologues, typical for systems having tilted smectic phases. For long homologues, its interesting feature is the parabolic

shape of *Sm-C* phase boundary. For long homologues, this phase as well as other tilted phase, *Sm-F*, become destabilized, in favor of *Sm-A* and *Hex-B* phase, respectively. In result, the *Sm-F* phase disappears for THI16. Resulting new triple point, *Hex-B* - *Sm-F* - *Sm-C*, is observed in binary mixtures. An unusual is the behavior of *Sm-C* phase. For long homologues, this phase does not vanish but its low and high-temperature limits are stabilized near 95 °C and 110 °C, respectively. The kink of the *Sm-C* - *Sm-A* phase transition line might suggest a differentiation between *Sm-C* phases for long (n>15) and shorter THIn homologues. However, on phase diagrams of binary systems, e.g. THI13-THI17, no kink appears.

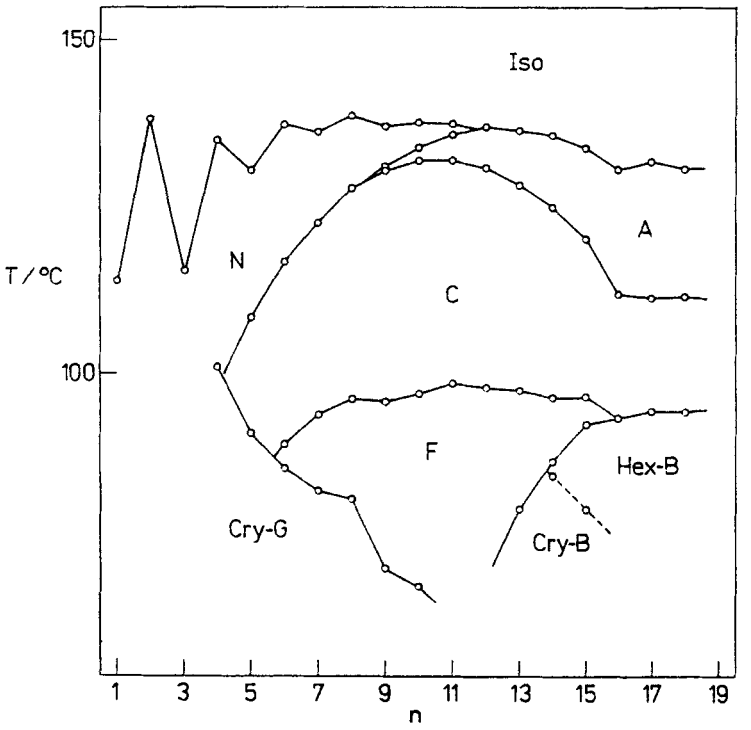


FIGURE 1 Phase diagram for homologous THI series.

Information about diagrams and phase transitions were completed by DSC and X-ray studies. For example, the presence of hexatic-*B* and crystalline-*B* phases in the THI series was established from binary phase diagram (Sect. 2.4.) and confirmed by X-ray scattering method. These phases do not differ in textures neither in homeotropic nor homogeneous orientation.

2.2. DSC studies

The main results are: (i) - *Sm-C* - *N* phase transition is first-order and its enthalpy increases with broadening nematic phase or, alternatively, with decreasing distance to more ordered *Sm-G* or *Sm-F* phases; (ii) - both *Sm-F* - *Sm-C* and *Hex-B* - *Sm-C* phase transitions are accompanied by strong pre-transitional anomalies in the specific heat; (iii) - *Cry-G* - *Sm-F* phase transition is first-order and its small enthalpy effect, which is controlled by temperature range of the hexatic phase, vanishes above a critical phase width; (iv) - *Hex-B* - *Sm-F* phase transition is accompanied by small thermal effects. For THI15, a jump in the specific heat, 016 $Jg^{-1}K^{-1}$, and, for THI14, a small peak with latent enthalpy of 0.10 Jg^{-1}, independent on the scanning rate, are observed (Figure 2).

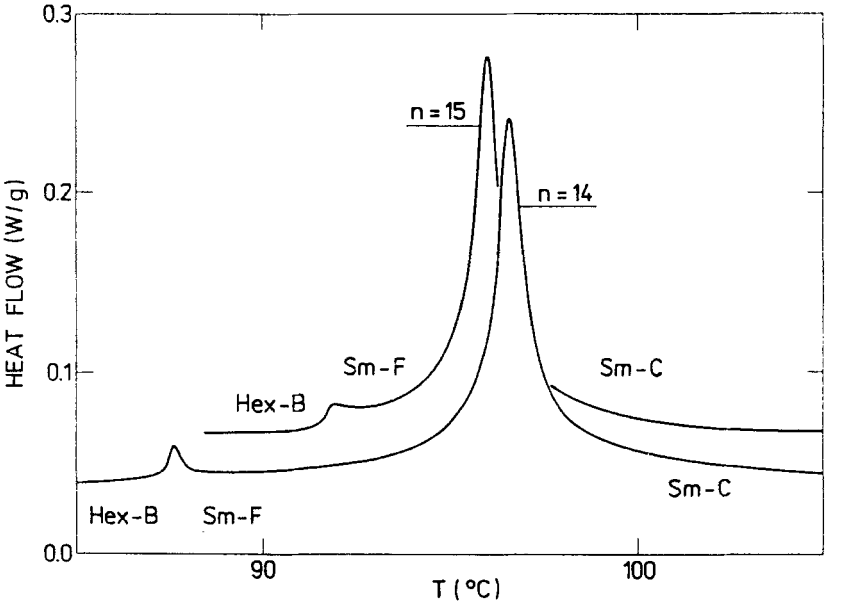


FIGURE 2 Thermograms of THIn compounds. Note different shape of heat flow signal at *Hex-B* - *Sm-F* phase transition for THI14 and THI15.

These results suggest, in agreement with optical studies, that the transition order is changed from continuous (case of THI15) to first-order (case of THI14) as the system moves between *Hex-B* - *Sm-F* - *Sm-C* and *Cry-B* - *Hex-B* - *Sm-F* triple points.

TABLE I. Temperatures (°C) and, in parentheses entalpies (J g^{-1}) of the phase transitions for the compounds of the THIn series.

n	*Cry*		*Sm-X*[a]		*Sm-F*		*Sm-C*		*Sm-A*		*N*		*Iso*
1	•	155.3 (126)									• 113.8 (1.0)		•
2	•	127.9 (92)									• 138.6 (2.9)		•
3	•	124.1 (76)									• 120.0 (1.8)		•
4	•	104.8 (52)	•	101.5 (19.8)							• 135.1 (3.9)		•
5	•	86.5	•	91.3 (6.8)			•	108.6 (8.4)			• 130.6 (3.1)		•
6	•	91.3 (44)	•	86.6 (4.7)[b]	•	90.2	•	116.8 (6.2)			• 137.2 (3.4)		•
7	•	92.9 (43)	•	82.7 (0.4)	•	94.4 (0.75)	•	122.8 (6.2)			• 136.3 (3.7)		•
8	•	87.4 (37)	•	81.6 (0.25)	•	96.2 (3.3)	•	128.0 (4.9)			• 138.7 (4.3)		•
9	•	62.7 (69)	•	71.6 (0.04)	•	96.6 (3.7)	•	130.5 (0.12)	•	130.9 (4.5)	• 137.3 (3.9)		•
10	•	81.2 (32)	•	68.4 (0.03)	•	97.0 (3.9)	•	131.4 (0.13)	•	133.8 (3.9)	• 137.7 (4.3)		•
11	•	79.5 (71)			•	98.4 (3.7)	•	131.2 (0.05)	•	136.0 (14.0)[b]	• 137.4		•
12	•	77.8 (44)			•	98.1 (4.2)	•	129.4 (0.06)	•	137.0 (14.6)			•
13	•	85.6 (78)	•	80.9 (0.06)	•	97.8 (3.8)	•	127.5 (0.01)	•	136.8 (14.2)			•
14	•	85.0 (74)	•	87.3 (0.10)	•	96.6 (4.4)	•	122.6	•	135.7 (14.5)			•
15	•	91.0 (84)	•	91.6 (0.16)[c]	•	96.0 (4.2)	•	120.1	•	134.2 (14.3)			•
16	•	88.9 (75)	•	92.9 (2.8)			•	111.8	•	131.0 (14.9)			•
17	•	94.8 (95)	•	94.5 (3.8)			•	110.6	•	131.9 (14.4)			•
18	•	95.2 (92)	•	94.1 (3.6)			•	110.7	•	130.9 (14.2)			•

[a] Cry-G (for n = 4 to 10); Cry-B (for n = 13) or Hex-B (for n = 14 to 18).
[b] total entalpy for unresolved peaks.
[c] specific heat change ($Jg^{-1}K^{-1}$).

2.3. X-ray studies

The layer spacing, d, thus molecular tilt, in long homologues of the THI series were determined by X-ray scattering method. Of our special interest were phase transitions involving hexatic phases and some relevant results are presented on Figure 3. The *Sm-F* - *Sm-C* phase transition was accompanied, in all studied

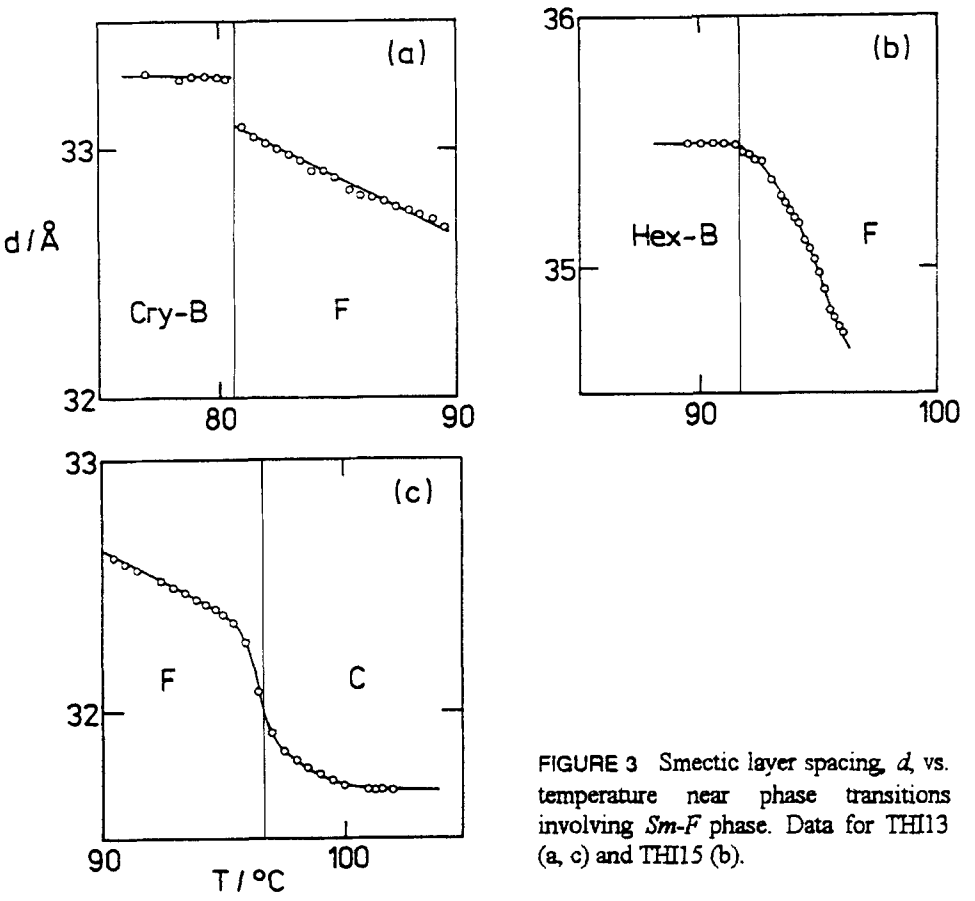


FIGURE 3 Smectic layer spacing, d, vs. temperature near phase transitions involving *Sm-F* phase. Data for THI13 (a, c) and THI15 (b).

compounds, by markedly increasing d. This fact explains the intensive motions visible on schlieren textures. Within the resolution limits of our X-ray machine, no discontinuity of layer spacing at this phase transition has been detected for all examined THIn compounds (discontinuities, if any, are below 0.02 Å). X-ray results confirm our suggestions that the character of the phase transition changes along *Sm-B* - *Sm-F* line. In THI13, a distinct jump in layer spacing was detected (Figure 3a) and the temperature hysteresis of d confirms first-order transition. For THI14, the layer discontinuity is comparable to the experimental resolution

limit, but, for THI15, it cannot be detected at all. Further, our results show that the *Hex-B - Sm-C* transition is also continuous. Surprisingly, not only layer spacing but also its slope seem to evolve continuously, like in the case of the *Sm-F - Sm-C* phase transition in THIn compounds. In smectic-*B* phase, the layer spacing is almost 1 A larger (at least for higher homologues) than in the *Sm-A* phase. E.g. for THI16, relevant values are 37.0 Å and 36.2 Å, respectively. It points probably to low orientational order in the *Sm-A* phase, and/or to some conformational disorder of alkoxyl chains at high temperatures.

2.4. Binary phase diagrams

Several binary phase diagrams were studied in order to identify the low-temperature orthogonal phase, as well as to confirm the presence and to locate new triple points. Some diagrams for binary systems of THI13 and THI14 with reference compounds having *Cry-B - (Hex-B -) Sm-A* phase sequence are presented on Figure 4. They reveal that, besides the hexatic phase, there is also crystalline-*B* phase present in the THI series. Temperatures of the *Cry-B - Hex-B* phase transition were determined from the extrapolation of the width of the hexatic phase to pure THIn compounds; they are shown on Figure 1.

In binary systems, the range of both tilted phases, *Sm-F* and *Sm-C*, has to decrease with increasing concentration of such reference compounds, which reveal only orthogonal phases. In result, there are two triple points, *Hex-B - Sm-F - Sm-C* and *Hex-B - Sm-C - Sm-A*, at the ends of the *Hex-B - Sm-C* transition line. All lines converging at these points might correspond to continuous phase transitions (with possible exception for theoretically first-order *Sm-F - Sm-C* transition[5]). For this reason, triple points are of special interest, because they might be new multicritical points, at which the three involved phases become asymptotically identical.

3. DISCUSSION AND CONCLUSIONS

Significant features of phase transitions between hexatically ordered and disordered smectic phases are the pretransitional anomalies in the specific heat. They result in more or less diffused DSC signals without, however, a noticeable peak rounding (cf. Figure 2). Such signals, easy to recognize, are not influenced

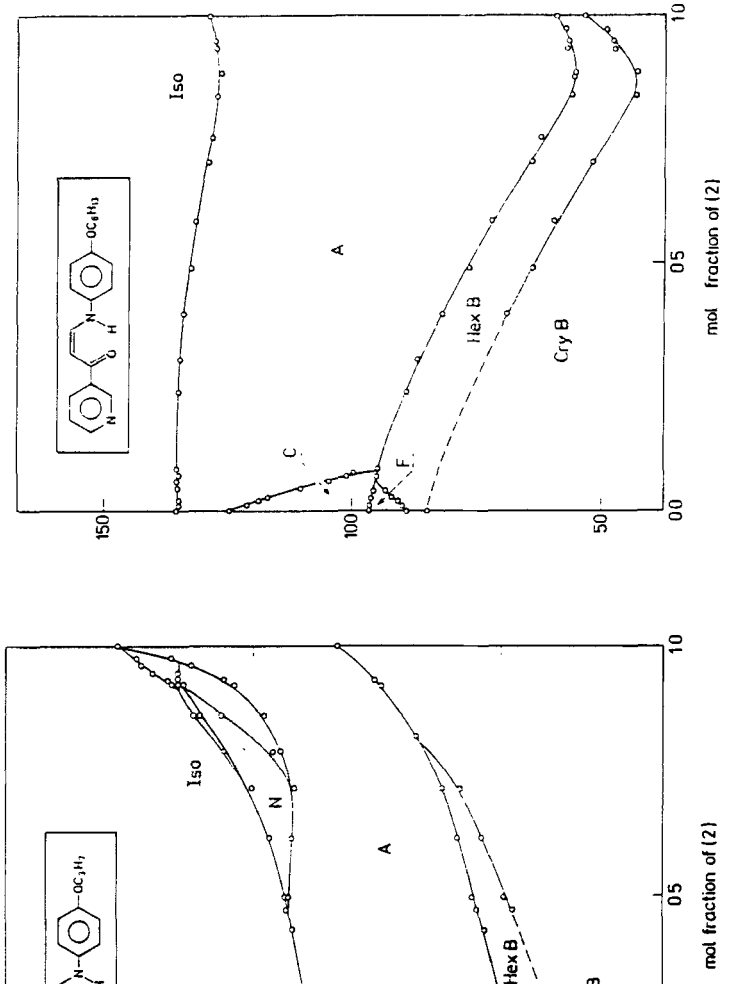


FIGURE 4. *Left:* phase diagram of binary mixtures of THI13 (1) with reference compound RF13 (2 - its formula is given with the inset). Note short *Hex-B* - *Sm-C* phase transition line between two triple points. Dashed line is *Cry-B* - *Hex-B* transition line obtained from extrapolation of the width of the *Hex-B* phase. *Right:* phase diagram for THI14 (1) - MPR6 (2) system.

by the molecular tilt, since their shape remain unchanged for tilted, orthogonal as well as mixed-tilt type transitions (among possible combinations, *Hex-B - Sm-A*, *Hex-B - Sm-C* and *Sm-F - Sm-C* transitions have been tested by us for several compounds). Broadened peaks were always found for systems having broad disordered smectic phase, *A* or *C*, if not being too close to crystal phases, *B* or *G*. Probably, more developed smectic layer ordering promotes more distinct changes of intermolecular distance at transition between disordered and hexatic smectics. Concomitant in-plane density changes are believed to be responsible for the specific heat changes.[2]

Some universal features seem to characterize phase transitions between hexatic phases, as well as between hexatic and crystalline phases. The thermal effects at the *Hex-B - Sm-F* and *Cry-B - Sm-F* transitions, observed for THI14 and THI13, respectively, are all of the same order. Thus we conclude that latent enthalpy is only weakly related to the building-up of the long-range positional order in systems with BOO. In fact, no measurable thermal effects ($\Delta H < 5$ mJg^{-1}) were detected at *Cry-B - Hex-B* phase transition in THI14. The effect of vanishing enthalpy has been previously observed in several crystalline - hexatic systems, both tilted[6] and orthogonal.[7] For some of these systems, strong discontinuities of in-plane correlation length, which confirm first-order transition, have been proved by high-resolution X-ray scattering method.[8]

Further examples of the evolution of phase sequences, similar to those observed for the THI series, may be obtained for some other chemically related compounds. We modified parent THI structure in two ways:

(i) - tolyl ring is introduced into molecules instead of 2-methylthienyl ring. In this case, the transition from tilted to orthogonal phases is also induced by long terminal alkoxyl groups. However, a crystalline-*B* phase appears instead of the hexatic-*B* phase and an additional, weakly-tilted intermediate phase (possibly *Sm-L*) intervenes between the smectic phases,[7] *F* and *B*;

(ii) - the second way is referred to thienyl compounds, mTHIX, with long alkyl substituent fixed instead of methyl group, but with alkoxyl replaced by a small halogen substituent X = F, Cl, Br, I. In this case the *Sm-A* phase is always present. However, the appearance of more ordered phases, orthogonal *Hex-B* and *Cry-B*, or tilted *Sm-F* and *Cry-G*, depends on the size of the substituent. For 6THII compound having hexyl (m=6) and iodo (X=I) terminal groups, mixed-tilt type phase sequence:

Cry-G -	*Sm-F* -	*Hex-B* -	*Sm-A* -	*Iso* phase
93.2	96.5	111.0	162.8	T(°C)

is observed. For this compound, the phase transition *Sm-F* - *Hex-B* seems to be continuous with a small decrease in the specific heat, ca. 0.03 $Jg^{-1}K^{-1}$, clearly seen on DSC thermograms. For a more bulky substituent, X = CF_3, smectic-*B* phases are overlapped by their tilted counterparts, what results in already known phase sequence *Cry-G* - *Sm-F* - *Sm-A*.[9]

Summing up, compounds of the THI series are first thermotropic liquid crystals, for which transition between tilted and untilted hexatic phases is reported. The orthogonal *Hex-B* phase appears, surprisingly, below tilted hexatic *Sm-F* phase, i.e. in an inverted phase sequence. Transition between these hexatic phases is either discontinuous or continuous, depending on the width of the *Hex-B* phase. The character of the layer spacing, or tilt changes, at this transition is different from that having a corresponding tilt-driven *Sm-C* - *Sm-A* transition between disordered smectics. In the hexatic system, no distinct pretransitional anomalies of the layer spacing are observed within the Sm-F phase. Close to the *Sm-F* - *Sm-C* - *Hex-B* triple point, found in binary mixtures, both *Hex-B* - *Sm-F* and *Hex-B* - *Sm-C* transitions seem to be continuous. It suggests that this triple point is a new multicritical point, even in the systems where phase transition *Sm-F* - *Sm-C* would be first-order, as predicted by the theory.[5] A normal phase sequence, with continuous phase transition from *Sm-F* to *Hex-B* phases on heating, has been found in pure mTHIX compounds.

4. EXPERIMENTAL

Enaminoketone thienyl derivatives, mTHIn and mTHIX, were synthesized in a routine way,[6] from appropriate 4-substituted-2-acetyl-thienyls and 4-substituted-alkoxylanilines, and products were carefully purified by crystallization. Chemical structures of both intermediates and final compounds were confirmed by elemental analysis, NMR and IR spectra.

Texture observations were performed with Jenapol-U polarizing microscope equipped with Mettler HT82 hot stage. Thermograms were taken using Perkin-Elmer DSC-7 at several scanning rates. Layer spacing was determined from X-ray scattering for homeotropically oriented samples, placed in double oven, with the wave vector accuracy of $1\ 10^{-3}\ A^{-1}$.

Acknowledgement

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