

# Liquid crystalline properties of new unsymmetrical compounds with benzothiazole core detected by TG/DSC-POM-XRD

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**Abstract** Thermal properties of two azomethine liquid crystals with a benzothiazole core were synthesized and investigated by applied Mettler-Toledo AG equipment (TG/DSC). Azomethines with benzothiazole core was obtained by nucleophilic addition of benzothiazole-2-carboxaldehyde in *N,N*-dimethylacetamide (DMA) solution with 4-(heptadecafluorooctyl)aniline (BTA1) or 4-hexadecylaniline (BTA2). The differential scanning calorimetry (DSC) was employed to evaluate their phase transitional behavior. Variable heating and cooling rates were used to study liquid crystalline properties of azomethines with benzothiazole core. Compound BTA1 exhibited liquid crystalline properties, while BTA2 is non-mesogenic. Three or four endothermic DSC peaks were observed for both compounds during heating process with the rate 0.5 °C/min. The mesophase was identified and confirmed by XRD study and polarized optical microscopy (POM) too. The thermal stability was determined by thermogravimetric analysis (TG). The temperatures of 5% mass loss ( $T_{5\%}$ ) of BTA1 and BTA2 range from 212 to 317 °C in nitrogen.

**Keywords** Azomethines · Imines · Liquid crystals · DSC

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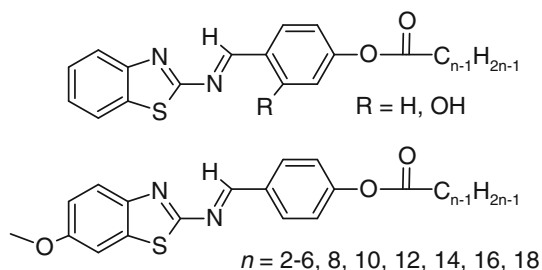
## Introduction

Azomethines called also imines are quite often investigated as liquid crystalline (LC) compounds [1–4]. Azomethine bond (HC=N) incorporated into the molecular structure cause increase the length and polarizability anisotropy of the molecular core in order to enhance liquid crystal phase stability. On the other hand, the incorporation more polarisable than carbon heteroatoms such as sulfur (S) and/or nitrogen (N) results in changes in LC phases and often in the physical properties of the mesophases [5]. The presence of benzothiazole ring with electron-rich sulfur atom in the organic compound structure can influence on decrease of the ionization potential of the sample and generate smectic phase [6, 7].

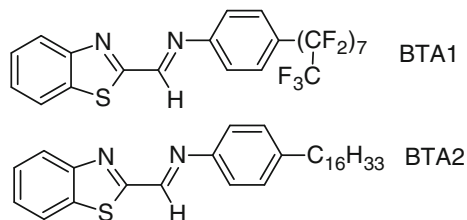
Among different structures of synthesized liquid crystalline azomethines compounds with benzothiazole ring are not widely investigated [6, 7]. General formulas of the compounds investigated previously by Ha et al. [6, 7] are depicted in Fig. 1.

Azomethines presented in Fig. 1 possess from 12 to 16 alkoxy chain lack of lateral hydroxyl group exhibited smectic A (SmA) phase, while those in the series with OH group were non-mesogenic [6, 7]. For the compounds with terminal methoxy group presented in Fig. 1 mesogenic properties were found for the length of chain higher than  $n = 3$ . Enantiotropic nematic phase was found for all investigated samples. The smectic C phase emerged from the decanoyloxy derivative onwards [6, 7].

On the other hand, the presence of fluorine substituent in organic compounds is very interesting because of the combination of polar and steric effects. The great strength of the C–F bond confers stability on fluorine substituted compounds [8]. Azomethines with fluorinated chains were not widely investigated, except our previously work [9–11] and



**Fig. 1** Chemical structure of azomethines with benzothiazole core and ester group



**Fig. 2** Chemical structure of azomethines BTA1 and BTA2 with benzothiazole core being the subject of this study

Bilgin-Eran et al. [12] study. The authors in [12] found that the thermal behavior of the semi-perfluorinated imines depends on the number of chains, the substitution pattern, and the number of fluorine atoms in the fluorine alkyl chains. Along with increasing the number of *F* atoms in the fluorine alkyl chains stabilization of smectic and columnar mesophases was observed [12]. We recently reported mesomorphic properties of unsymmetrical imines based on 4-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptafluoroundecyloxy) benzaldehyde [9, 10] or 4-biphenyl carboxaldehyde [11]. An enantiotropic smectic phases were observed for all the systems studied.

Small organic compounds and polymers exhibited liquid crystalline properties have attained wide interest in recent years due to their great potentials in different devices, as well as other applications in high-performance materials [13–17].

The aim of this study was to characterize the mesomorphic properties of the two representatives of imines with benzothiazole core. These investigations were carried out with DSC, POM, and XRD studies. Chemical structure of the azomethines investigated in this study is presented in Fig. 2.

Azomethines investigated in this study in contrary to compounds described in [6, 7] were obtained from aldehyde with benzothiazole ring (benzothiazole-2-carboxaldehyde).

## Experimental

Phase transition temperatures and enthalpy changes were measured using Mettler-Toledo AG (DSC) at different

heating and cooling of 10, 5, 1, 0.5 °C/min and –10, –5, –1, –0.5 °C/min rates, respectively. Moreover, the sample was three times heating and cooling with the same rate (5 °C/min) in air and nitrogen atmosphere. The samples of 9–11 mg were placed in ceramic crucible in a nitrogen atmosphere.

Thermogravimetric analyses (TG) were performed on a Mettler-Toledo AG apparatus at a heating of 5°/min rate under nitrogen.

Polarizing optical microscope (ECLIPSE MA 200, Nikon) was used for preliminary studies of the texture of liquid crystals. Textures exhibited by the compounds were observed using polarized light with crossed polarizers. Samples were prepared as solid sandwiched between a glass slide and a cover slip.

X-ray diffraction studies were performed on Bruker D8 GADDS system (CuK $\alpha$  radiation, Vantec 2000 area detector), equipped with Linkam heating stage. Samples were prepared in a form of a droplet on heated surface.

Benzothiazole-2-carboxaldehyde (1 mmol) and 4-(heptafluorooctyl)aniline (1.5 mmol, BTA1) (or 4-hexadecylaniline (1.5 mmol, BTA2)) were refluxed for 10 h in *N,N*-dimethylacetamide (10 mL, DMA) in the presence of *p*-toluenesulfonic acid (0.06 g, PTS). After cooling, the mixture was precipitated with 50 mL of methanol. The crude product was washed three times with methanol (3  $\times$  50 mL) and next two times with acetone (2  $\times$  35 mL) to remove unreacted monomers. The compounds were recrystallized from *n*-hexane. BTA1 (*N*-[(*E,Z*)-1,3-benzothiazol-2-ylmethylidene]-4-(heptafluorooctyl)aniline) was obtained as pale-yellow long needles, while BTA2 (*N*-[(*E,Z*)-1,3-benzothiazol-2-ylmethylidene]-4-hexadecylaniline) existed as beige solid. Both compounds were obtained with very good yield (90%). The purity of both compounds was checked by thin layer chromatography (TLC, Merck, silica gel *F*254) and visualized under UV light.

## Results and discussion

The thermal properties of BTA1 and BTA2 were characterized by both differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). The thermal stability of both compounds was detected by TG performed in a nitrogen atmosphere at a heating of 5 °C/min rate to 800 °C. The results of thermogravimetric analysis are presented in Table 1.

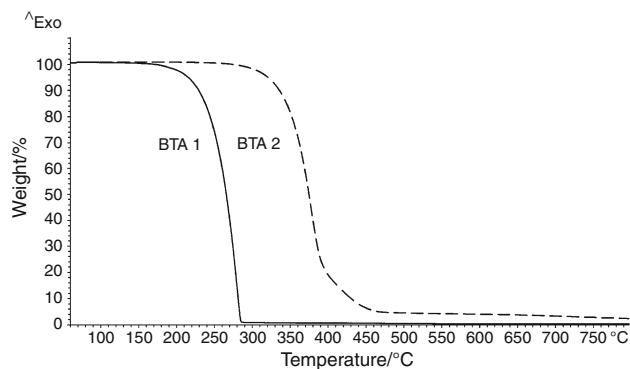
The TG curve of both azomethines (Fig. 3) indicates one main reaction stage. It is clear that the thermal properties of organic compounds depended strongly on the structure, in this case on the microstructure of the compound backbone. The initial decomposition based on 5% mass loss and the temperature at which 10% mass loss

**Table 1** Thermal stability of BTA1 and BTA2

Code	$T_{5\%}/^{\circ}\text{C}^{\text{a}}$	$T_{10\%}/^{\circ}\text{C}^{\text{a}}$	$T_{25\%}/^{\circ}\text{C}^{\text{a}}$	Char yield/% <sup>b</sup>
BTA1	212	228	249	0.1
BTA2	317	334	357	2.2

<sup>a</sup>  $T_{5\%}$ ,  $T_{10\%}$ ,  $T_{25\%}$ : temperatures at 5, 10, 25% mass loss, respectively

<sup>b</sup> Residual mass when heated to 800 °C in  $\text{N}_2$

**Fig. 3** Thermogravimetric analysis of BTA1 and BTA2 in  $\text{N}_2$  atmosphere

occurred, which is usually considered the criterion for assessing the thermal stability, lay within the range of 212–317 °C and 228–334 °C, respectively (Table 1).

Our study showed that compound BTA2 with aliphatic chain started to decompose at a higher temperature (317 °C) than BTA1 with fluorinated chain. Moreover, taking into account the amount of carbonized residue, significant differences between BTA1 and BTA2 were found. The char yield percent at 800 °C in the compound BTA2 was higher (2.2%) than in BTA1 (~0.1%). TG results of the azomethines showed that obtained small organic compounds BTA1 and BTA2 had quite good thermal stability.

The phase transition temperatures and corresponding enthalpy changes of azomethines BTA1 and BTA2 determined using Mettler-Toledo AG (DSC) at heating of 10, 5, 1, and 0.5 °C/min rates in nitrogen (and air) atmosphere are summarized in Tables 2 and 3. DSC heating curves of BTA1 and BTA2 are shown in Figs. 4 and 5. Compound BTA1 exhibited liquid crystalline properties, while BTA2 is non-mesogenic.

DSC studies revealed that the compound BTA1 exhibited a clearing point temperature higher than 179 °C and quite broad temperature range of the mesophases (~9 and 37 °C). On the other hand, BTA2 showed temperature of isotropisation lower than 105 °C. Differences in liquid crystalline properties of BTA1 and BTA2 are clear observed. The presence of fluorine atoms in BTA1 caused increases the value of temperature of isotropisation and appearance of mesophase in comparison with BTA2.

To investigate liquid crystalline properties of azomethines BTA1 and BTA2 a variable heating (cooling) rate study was performed (Table 2).

**Table 2** Transition temperatures and associated enthalpy changes of BTA1 and BTA2 upon first heating and cooling with different rate (in  $\text{N}_2$ )

Conditions	Transition temperatures/ $^{\circ}\text{C}$ ( $\Delta H/\text{J}$ )	
	BTA1	BTA2
Heating <sup>a</sup>	137.5, 142.7 (0.37), 179.8 (0.05)	63.6, 84.7 (0.90)
Cooling <sup>a</sup>	128.5 (0.31), 178.3 (0.08)	67.1 (0.86)
Heating <sup>b</sup>	138.0, 143.1 (0.36), 180.3 (0.05)	63.7 (0.04), 84.4 (0.61)
Cooling <sup>b</sup>	126.0 (0.27), 179.7 (0.06)	65.4 (0.67)
Heating <sup>c</sup>	136.2 (0.09), 142.4 (0.28), 180.2 (0.08)	63.2 (0.06), 83.8 (0.73)
Cooling <sup>c</sup>	125.6 (0.27), 152.9 (1.31), 179.5 (0.06)	64.9 (0.86)
Heating <sup>d</sup>	104.5 (0.49), 133.3 (0.13), 142.2 (0.25), 180.0 (0.05)	63.3 (0.05), 83.8 (0.62), 104.6 (0.12)
Cooling <sup>d</sup>	126.4 (0.21), 179.2 (0.03)	69.7 (0.87)

<sup>a</sup> Heating/cooling rate 10 °C/min

<sup>b</sup> Heating/cooling rate 5 °C/min

<sup>c</sup> Heating/cooling rate 1 °C/min

<sup>d</sup> Heating/cooling rate 0.5 °C/min

**Table 3** Transition temperatures and associated enthalpy changes of BTA1 and BTA2 upon first, second, and third heating and cooling rate at 5 °C/min in air and in nitrogen

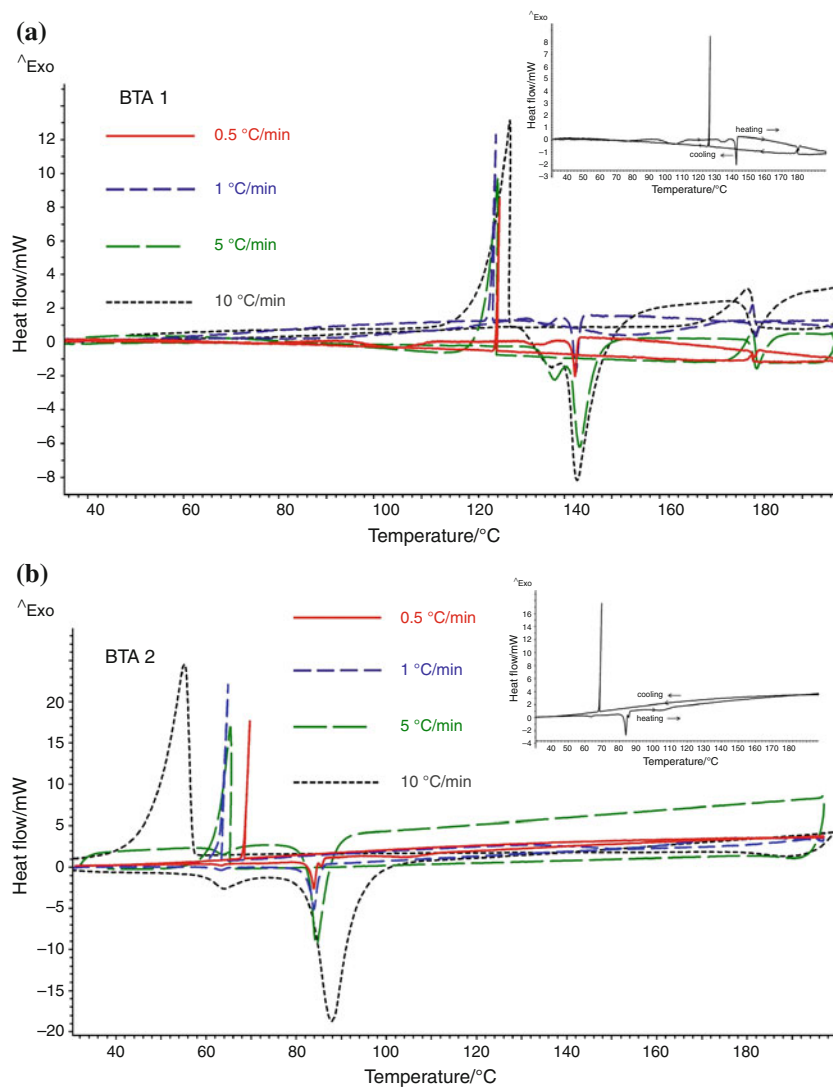
Conditions	Transition temperatures/ $^{\circ}\text{C}$ ( $\Delta H/\text{J}$ )	
	BTA1	BTA2
In air		
Heating <sup>a</sup>	136.3, 142.6 (0.37), 180.4 (0.07)	63.7 (0.06), 84.4 (0.77)
Cooling <sup>a</sup>	128.7 (0.31), 179.3 (0.07)	65.1 (0.82)
Heating <sup>b</sup>	142.6 (0.30), 180.3 (0.07)	77.6, 84.2 (1.08)
Cooling <sup>b</sup>	126.9 (0.30), 179.4 (0.07)	65.3 (0.84)
Heating <sup>c</sup>	142.7 (0.29), 180.3 (0.07)	77.5, 84.0 (1.04)
Cooling <sup>c</sup>	127.4 (0.29), 179.3 (0.07)	65.3 (0.84)
In $\text{N}_2$		
Heating <sup>a</sup>	135.9, 142.8 (0.37), 180.1 (0.04)	63.8 (0.06), 84.7 (0.74)
Cooling <sup>a</sup>	126.6 (0.31), 178.8 (0.07)	67.6 (0.84)
Heating <sup>b</sup>	142.4 (0.30), 180.1 (0.06)	77.4, 84.3 (0.73)
Cooling <sup>b</sup>	125.7 (0.30), 178.7 (0.07)	67.5 (0.85)
Heating <sup>c</sup>	142.4 (0.31), 180.1 (0.07)	77.4, 84.3 (0.77)
Cooling <sup>c</sup>	124.7 (0.30), 178.8 (0.07)	66.8 (0.85)

<sup>a</sup> First run

<sup>b</sup> Second run

<sup>c</sup> Third run

**Fig. 4** DSC traces of the BTA1 (a) and BTA2 (b) upon first heating and cooling at 10, 5, 1, and 0.5 °C/min rate in nitrogen (inset presented DSC traces of compounds upon heating and cooling at 0.5 °C/min rate)

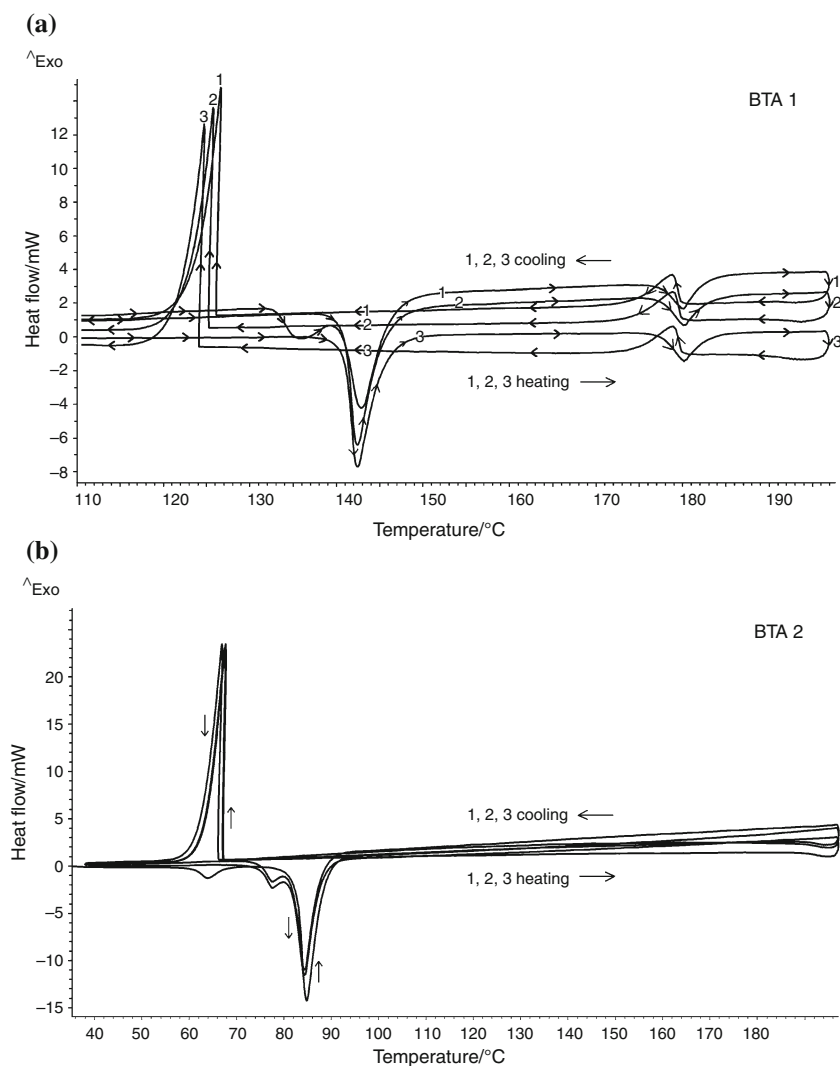


DSC trace of the BTA1 during heating at 10 °C/min showed three main peaks with maxima at 137.5, 142.7, and 179.8 °C with  $\Delta H = 0.37$  J and 0.05 J, respectively. During heating of the BTA1 at 5 and 1 °C/min also three peaks was noted almost at the same temperature values (see Table 2). Decreasing the value of heating from 10 to 1 °C/min not caused big changes in DSC traces of BTA1 (Table 2; Fig. 4a). Differences start to be observed when the heating rate was 0.5 °C/min. The first endothermic peak during heating of the BTA1 at 0.5 °C/min appeared at 104.5 °C with enthalpy change 0.49 J. Azomethine BTA1 showed four endothermic transitions (at heating rate 0.5 °C/min), the transition at 104.5 and 133.3 °C was the melting of aliphatic and aromatic part, respectively, and the third and fourth transitions correspond to mesophase transitions (Table 2). These transitions were thermo reversible (see Table 2).

Compound BTA2 during heating cycles at 10, 5, and 1 °C/min exhibited two main endothermic peaks almost at the same temperature value (see Table 2; Fig. 4). Differences were found during heating rate of BTA2 at 0.5 °C/min. DSC curve of BTA2 showed three transitions at heating rate 0.5 °C/min. Additional peak at 104.6 °C with enthalpy change 0.12 J appeared similar as in the case of BTA1. During cooling of the BTA2 sample only one exothermic peak appeared independent on the cooling rate (Table 2).

The transition temperature is strongly depended on the kind of aliphatic chain and in our cases transition temperatures of BTA2 are lower than that of BTA1 (Table 2). The values of enthalpy change were higher for BTA2 than for BTA1 (Table 2). This behavior is caused by the presence in the structure of BTA1 fluorine atoms in aliphatic chain (see Fig. 2). The bulky nature of the neighboring fluorine

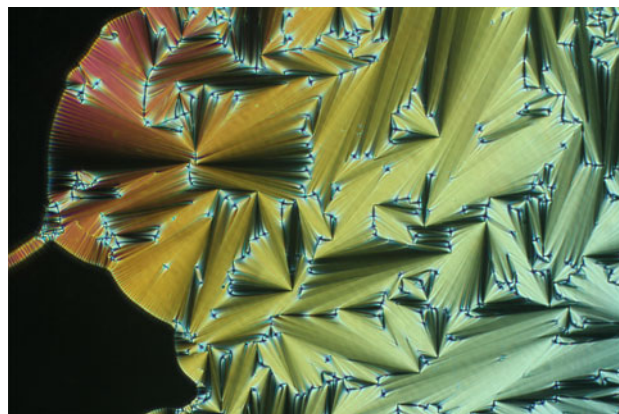
**Fig. 5** DSC heating curves of BTA1 (a) and BTA2 (b) upon first, second, and third heating and cooling at rate equal to 5 °C/min in nitrogen



substituents causes steric interactions which tend to limit conformational flexibility and for this reason the perfluorine chains are often described as stiff [8].

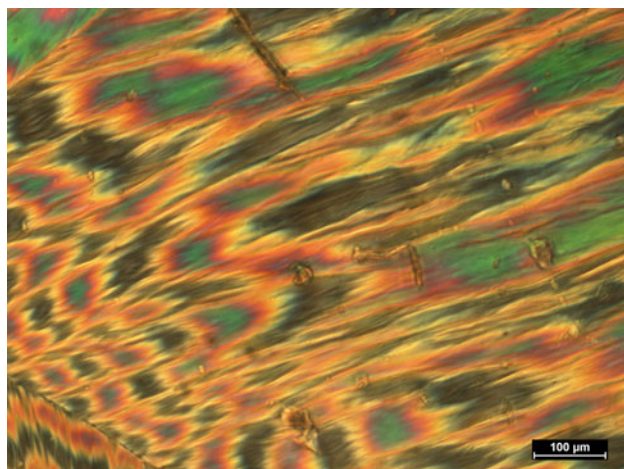
Moreover, compounds BTA1 and BTA2 were investigated during first, second, and third heating and cooling scan at 5 °C/min at N<sub>2</sub> and air atmosphere (Table 3).

No big changes in values of temperature and enthalpy change were observed during first, second, and third heating and cooling scans in air and nitrogen atmosphere. Both compounds exhibited very similar thermal behavior in air and nitrogen atmosphere (Table 3). These observations confirm that the thermal history of both compounds is stabilized. DSC heating curves of BTA1 and BTA2 upon first, second, and third heating and cooling at rate equal 5 °C/min in nitrogen are shown in Fig. 5.



**Fig. 6** Characteristic texture of the mesophase observed on cooling of BTA1 compound: SmA

The mesophases of both compounds were observed preliminary under polarizing optical microscopy (POM). Observation of BTA1 under POM upon cooling from its isotropic liquid phase showed the presence of one mesophase, probably smectic A phase. POM microphotographs of BTA2 show spherulite-type morphology. The optical



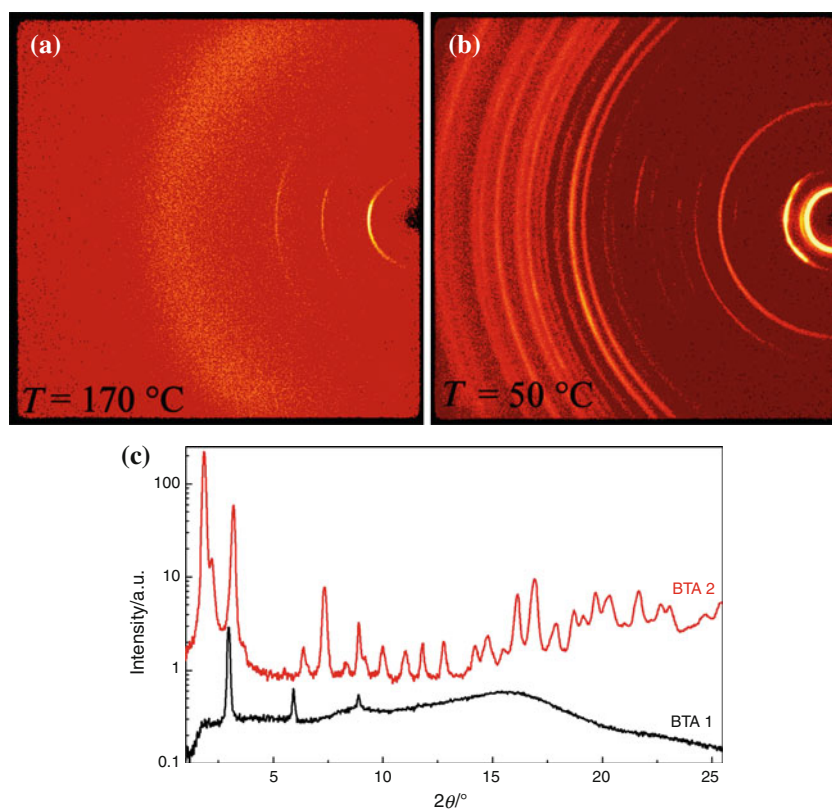
**Fig. 7** Optical photomicrographs of BTA2 taken during the cooling cycles: spherulite-type texture

photomicrographs of azomethine BTA1 and BTA2 are depicted in Figs. 6 and 7.

In order to confirm the presence of mesophases in BTA1 and BTA2, X-ray diffraction (XRD) analysis was performed. Figure 8 shows XRD patterns for BTA1 compound in SmA phase (a) and BTA2 compound in crystalline phase (b). By the integration of above patterns over azimuthal angle the dependence of the diffracted intensity on the diffraction angle  $2\theta$  was obtained (Fig. 8c).

X-ray diffraction experiments revealed mesogenic nature of the BTA1 compound, which shows enantiotropic smectic A phase (SmA). X-ray pattern registered at 170 °C exhibits series of three sharp, commensurate reflections at low angles region and a diffused one at higher angles (Fig. 8); such a pattern is characteristic for lamellar (smectic) structure. Smectic layer thickness calculated from the position of low angle signals is 29.8 Å, which is considerably more than estimated molecular length (23 Å in most extended conformation). This suggest the partially bilayer structure of the smectic phase (SmAd); because of the presence of thick, perfluorinated chain in the molecules of BTA1 one can assume that molecules from neighboring layers overlap their aromatic parts to fill the space effectively. Broad diffused signal in high angle region of the XRD pattern correspond to the periodicity 5.6 Å, which is the mean distance between perfluorinated chains. Contrary

**Fig. 8** 2D XRD patterns for **a** BTA1 compound in SmA phase and **b** BTA2 compound in crystalline phase. By the integration of above patterns over azimuthal angle the dependence of the diffracted intensity on the diffraction angle  $2\theta$  is obtained (c)



to BTA1, compound BTA2 does not form liquid crystalline phase, the first phase appearing on cooling the isotropic liquid gives the XRD pattern typical for crystalline phase (Fig. 8), with number of sharp signals in the whole angle range.

## Conclusions

The mesomorphic behavior of two azomethine liquid crystals with a benzothiazole core was investigated by DSC-POM-XRD experiments. The presence of fluorine atoms in BTA1 caused increasing the transition temperature to isotropic phase ( $I \sim 179$  °C) in comparison with BTA2 ( $I < 105$  °C). BTA1 exhibited enantiotropic smectic A phase while for BTA2 only spherulite-type morphology was observed. The thermal history of both compounds is stabilized. No big differences in transition temperatures and enthalpy change were observed during first, second, and third heating and cooling scans in air and nitrogen atmosphere. BTA1 and BTA2 had quite good thermal stability with a 5 wt% loss temperature at about 212 and 317 °C, respectively.

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