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Time-Resolved Study of the Phase Transition of 4-Octyloxy-4′Cyano-Biphenyl by Small Angle X-Ray Scattering

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Polymorphisms of 4-octyloxy-4′cyano-biphenyl was studied by differential scanning calorimetry and time-resolved small angle X-ray scattering. The X-ray scattering identified a new phase and indicated that the crystalline structure of the needle form was different from those reported in literatures. Upon heating, parallel transformations of the needle form into a stable crystal and into smectic phase were observed by the time-resolved scattering, while transformation of the new phase into smectic phase was found absent at low temperatures and the parallel transformations of the new phase into the stable crystal and into smectic phase occurred only at higher temperatures.

Keywords: 8OCB; phase transition; polymorphism; SAXS

1. INTRODUCTION

Crystalline polymorphism of alkoxy-cyanobiphenyls (nOCB) is interesting and attracted quite a few studies [1–6]. For 4-octyloxy-4′ cyano-biphenyl (8OCB), three metastable crystal forms and one stable crystal form have been reported [2–4]. The metastable crystals could be of square plate, parallelepiped, or needle form, and their single crystals have been obtained by careful crystallization from solvent mixtures at controlled temperatures. The single crystals simplified the differential scanning calorimetry (DSC) study of the transformation between the metastable phases and the stable phase and the determination of the crystallographic structure of the polymorphism was also benefited from the accessibility of the single crystals. While

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most studies take advantage of the accessibility of the single crystals, the study of the behavior of mixture of different forms of crystal and liquid crystalline phases attracted less attention, and therefore, was less understood.

By dipole interaction between the nitrile bonds, alkoxy-cyanobiphenyls tend to associate as antiparallel pairs in liquid crystalline and crystalline phase. The length of the antiparallel pairs is slightly less than twice the length of a single molecule [7] and falls in the range of few nanometers, to which small angle X-ray scattering (SAXS) is accessible. The crystalline structures of the polymorphism of 8OCB have been studied by X-ray diffraction focusing on high scattering angles and in complement SAXS is expected to provide important information in the dimension of nanometers, which were probably missed or sometimes inaccessible in X-ray diffractions. The polymorphism of nOCB was also frequently studied by DSC which provided the temperature and latent heat of phase transition, but unable to provide clear information about the transformation between different polymorphism phases, especially when overlapped peaks of phase transition occur. To unveil the crystalline structures in nanodimension and to obtain a clearer picture for the phase transition between polymorphisms of 8OCB, we performed time-resolved SAXS experiments with synchrotron X-ray source to observe the crystalline structural change with rising temperature for samples of mixed crystallites and smectic liquid crystal. 8OCB is known to have one stable crystal form and three metastable crystal forms which include needle, parallelepiped, and square plate form. Our synchrotron scattering identified a new phase and found new characteristics of the crystalline structure for the needle form when the smectic phase also presented. Different polymorphisms were found coexisting in a heating process and their fractions, which evolved in the process, could be obtained from SAXS patterns to clarify the mode of the transformation between these phases.

2. EXPERIMENTAL

8OCB was obtained from Aldrich and used directly in this study. The behavior of phase transition of 8OCB was investigated using a differential scanning calorimeter (Pyris 1, Perkin Elmer). The time-resolved small angle SAXS experiments were performed in National Synchrotron Radiation Research Center, Hsinchu, Taiwan. A two-dimensional CCD detector (MARCCD165, MAR Inc., USA) was employed to capture the scattering patterns at a rate of 30 seconds per frame. The patterns in this study were isotropic and intensity

averaged over the whole range of azimuthal angle was reported. Liquid cell for DSC measurement (TA instruments) was used as the sample cell. By punching a hole on both the cover and bottom plate and covering the holes by Kapton film, X-ray was allowed to transmit the sample through the holes. A hot-stage (FP84 Mettler-Toletro) was used to control the heating and cooling rate, and at a fixed heating rate, the time-resolved measurement was equivalent to a temperature-resolved one. To obtain an appropriate scattering intensity, the relatively large amount of 8OCB was loaded in the cell and thermal gradient between the bulk and the detector, and hence induction of temperature lag was expected.

3. RESULTS AND DISCUSSION

Shown in Fig. 1 is the DSC trace of 8OCB. The measurement was preceded by a cooling process from 90°C, at which 8OCB is isotropic, to 30°C at a rate of 5°C/min followed by an isothermal process at 30°C for 10 minutes. An endothermic peak was observed at 45.5°C trailed by an exothermic dip at 46°C, which was then followed by a broad endothermic peak at 51.8°C overlapped with the last peak at 54.4°C. The smectic/nematic and the nematic/isotropic transformation temperature were determined to be 67 and 80°C, respectively,

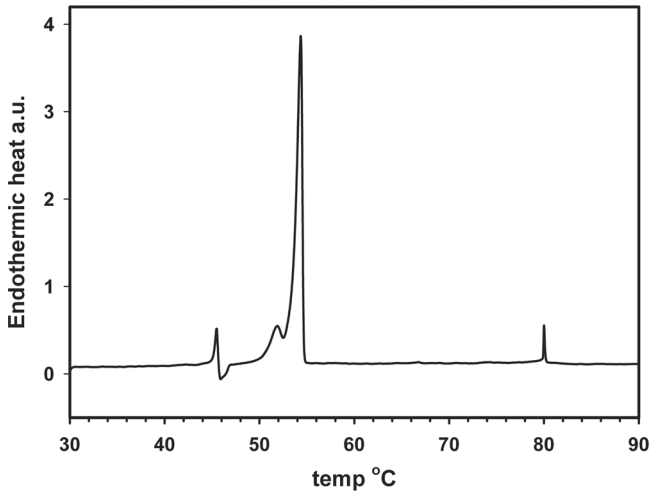

FIGURE 1 The DSC trace of 8OCB at a heating rate of 2°C/min. The heating was preceded by a process cooling from 90°C at a rate of 5°C/min and holding at 30°C for 10 minutes.

from the DSC trace by the locations of the corresponding endothermic peaks. For endothermic behavior of a commercial sample below 60°C, Jain et al. [3] reported the similar sequence of phase transformations with transition temperatures nearly duplicating ours. They suggested that these transition temperatures were characteristics of three different solid crystalline forms of 8OCB. Hori and Wu [4] investigated the melting behavior of a single crystal of the needle form of 8OCB. They reported that the metastable crystal melted at 50°C and transformed into crystal of a stable form whose melting point was at 53°C. They also investigated the melting behavior of a single crystal of another metastable polymorphism, the parallelepiped form, and found that the crystal had a melting peak at about 45°C and depending on the rate of heating the crystal transformed into needle and the stable form at different portions. Comparing our results with the previous reports, three different crystalline forms are concluded: first, the peak at 45.5°C is related to the melting of the parallelepiped crystallites; second, the peak at 51.8°C should be the melting peak of the needle crystallites, and the last peak at 54.3°C exhibits the melting of crystallites of the stable form. That the temperatures at the melting peaks are reported in our work instead of the temperatures where melting starts is responsible for the temperature differences. The conclusion implies the presence of at least three different crystal forms and possible transition between the crystal forms during the heating process.

Shown in Fig. 2 are selected SAXS patterns at temperatures between 61 and 84°C for 8OCB sample with the same thermal histories as that in DSC measurement. It is clearly seen from the figure that the diffraction peak at the scattering vector length or q of $1.98\,\mathrm{nm}^{-1}$ persists its presence until temperature exceeds 67°C. The peak is a signature of smectic phase of 8OCB since 67°C is the smectic-nematic transition temperature which is clearly indicated in the DSC trace in Fig. 1. The location of the peak reveals that the period of the layer structure of the smectic phase is 31.7 Å, which is very close to the measurements from previous works [7,8]. The period implies a bilayer stacking of the smectic phases [7–10] and the existence of antiparallel associated pairs [8]. Careful inspection to Fig. 2 reveals that the peak is in fact sitting on a broad hump of low height spreading from $q = 1.2$ to $3.3\,\mathrm{nm}^{-1}$. The hump consistently shows up as the temperature rises to 67°C which is the transition temperature of smectic to nematic phase and with the shifting of the center to higher q value, the hump still survives at temperatures higher than 80°C where the disorder phase starts to dictate. The hump could be related to the scattering originated from the pair correlation in longitudinal direction of the antiparallel associates since the corresponding dimension from the q range of the

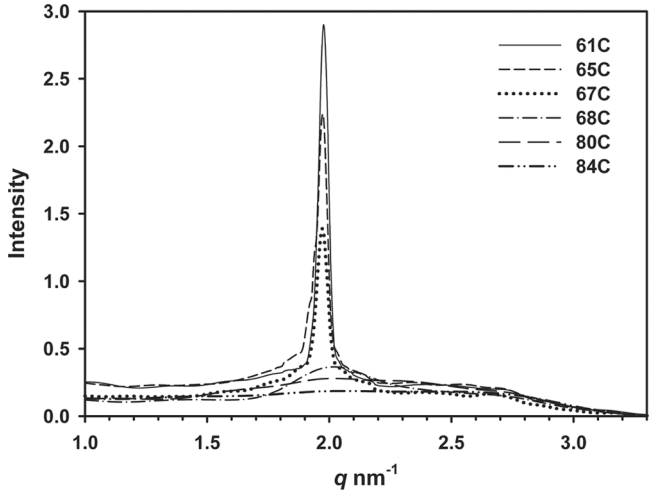

FIGURE 2 Selected SAXS patterns for smectic, nematic, and isotropic phase of 8OCB in a heating process. The heating rate was 2°C/min, and the heating process was preceded by a process cooling from 90°C at a rate of 5°C/min and holding at 30°C for 10 minutes.

hump is close to the axial dimension of the associates and its persistent presence in liquid crystalline phases and disorder phase.

Results of real-time SAXS investigation on the sample with the same thermal histories as that in the DSC measurement are shown in Fig. 3. At lower temperatures, the peaks of the smectic phase can be identified in the scattering patterns shown in the figure, though the peaks at some temperatures may be very small, and some even immerge into others. Thus the smectic phase coexisted with other crystalline phases between 31 and 61°C. The scattering patterns at 31°C and 45°C were essentially indistinguishable indicating the absence of phase changes in the range between these two temperatures. The patterns showed two distinct diffraction peaks at $q = 2.24\,\mathrm{nm}^{-1}$ and $3.18\,\mathrm{nm}^{-1}$ and a small broad peak at about $2.0\,\mathrm{nm}^{-1}$. The former two peaks are associated to a crystal different from the crystal to which the last peak is related, since the two changed synchronically with rising temperature, and the last behaved independently. The last peak could be a composite of the smectic peak at $1.98\,\mathrm{nm}^{-1}$ and the tail of a peak at $2.14\,\mathrm{nm}^{-1}$. The peak at $2.14\,\mathrm{nm}^{-1}$ corresponds to the crystal of the stable form which will be discussed in the next paragraph. At 46°C, the intensities of the peaks at $2.24\,\mathrm{nm}^{-1}$ and $3.18\,\mathrm{nm}^{-1}$ started diminishing; with increasing temperature they kept diminishing and,

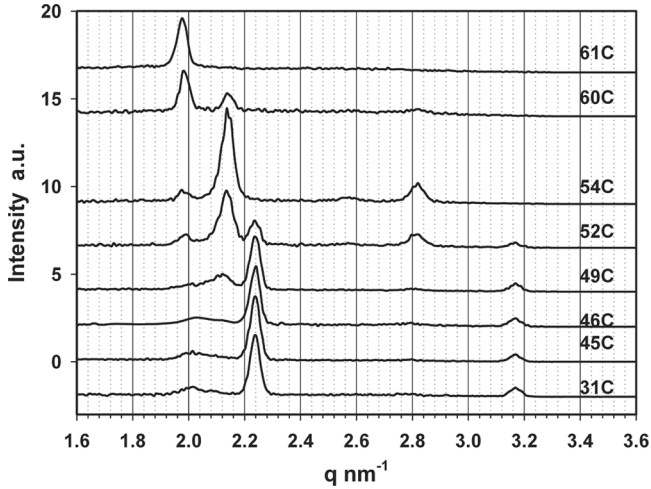

FIGURE 3 Selected SAXS patterns of 8OCB sample in a heating process. The heating rate was 2°C/min, and the heating process was preceded by a process cooling from 90°C at a rate of 5°C/min and holding at 30°C for 10 minutes.

finally, reached an undetectable value at 54°C to indicate the completion of a transformation. These two peaks could be the signatures of the needle crystallites of 8OCB because the temperatures at which they emerged and disappeared are consistent with the observations for the crystallites in DSC. Nevertheless, the crystallographic information revealed by our SAXS results was inconsistent with those in literature. The needle phase has been reported to assume a triclinic crystal structure with lattice parameters of $a = 12.710$ Å, $b = 20.410$ Å, $c = 7.325$ Å, $\alpha = 99.86^{\circ}$, $\beta = 99.44^{\circ}$, and $\gamma = 92.55^{\circ}$ [2]. The parameters predicted a spacing of $d_{100} = 12.50$ Å, $d_{010} = 20.05$ Å, and $d_{001} = 7.106$ Å. The second d spacing matched the peak at $q = 3.18\,\text{nm}^{-1}$ in our SAXS patterns and the peak at $2.24\,\text{nm}^{-1}$ can never match any prediction from the parameters, because $2.24\,\text{nm}^{-1}$ corresponds to a dimension of 28.05 Å, which is far larger than those of three edge lengths of the reported unit cell. The value of 28.05 Å is close to the quadruple of the value of lattice constant c. The reported lattice constants were derived from the X-ray diffraction data of a single crystal of the needle form, while our SAXS data were taken from a mixture of three different phases. We speculate that the presence of the smectic phase and crystals of the stable form could distort the needle crystals and results in the formation of super-lattice with a period of about 4 times the original value in c axis direction.

While the peaks of the needle crystal were diminishing, there emerged simultaneously three peaks located at 2.14, 2.58, and $2.85\,nm^{-1}$, though the last was uneasy to identify due to its small height. The intensities of the peaks grew as temperature increased, then decayed and, finally, disappeared at 61°C. The peaks were assigned to the crystal of the stable form by comparison of the characteristic temperatures with those in DSC experiments as well as the crystalline structure reported in the literature. Hori et al. [1] reported that the stable phase of 8OCB assumed a monoclinic crystal structure with the lattice parameters of $a = 30.56$–$30.62\,Å$, $b = 7.39$–$7.44\,Å$, $c = 25.43$–$25.52\,Å$, and $\beta = 107.3$–107.8°. The lattice parameters give inter planar spacings of $d_{100} = 29.2\,Å$, $d_{001} = 24.3\,Å$, and $d_{101} = 22.3\,Å$, and the corresponding scattering vector lengths for the spacings exactly match our peak locations. Considering the spacing of 29.2 Å, the molecules in the crystallites of the stable form could probably still assume an antiparallel pair packing.

Though the DSC traces declared the existence of the parallelepiped crystallites in the tested 8OCB sample at low temperatures, our SAXS patterns did not reveal any signal related to the crystal. The absence of the signal may be resorted to the extremely small amount of the crystallites or alternatively to the small dimensions of the unit cell which can be only detected in higher scattering angles.

The transition between the different crystal forms and smectic phase could be more clearly seen in Fig. 4 which shows the fraction of each phase throughout the heating process. The fractions were estimated from the contribution of each phase to the invariant Q, the total scattering power, of the tested sample. It is easier to interpret the figure by dividing it into three regions. In region I, where the temperatures are below 44°C, the coexistence of the stable, the needle, and the smectic phase was clearly seen, and there were essentially no changes in the composition of the sample as mentioned previously; in region II, which covers temperatures between 44°C and 54°C, when temperature increased, the fractions of the smectic phase and crystal of the stable form grew, and the needle crystal started to reduce its fraction at 44°C and disappeared at 54°C. Because the melting temperature of the stable crystal matches the upper bound of this region, the crystal could not melt into smectic phase in this region and consequently, we concluded that increase in the content of the smectic phase and the stable crystal solely came from the melting of the needle crystal, which implies that there were two processes occurring in parallel: one is the direct melting of the needle crystal into smectic phase, and the other is transformation of the needle crystal into the stable crystal; while in region III, where temperatures are

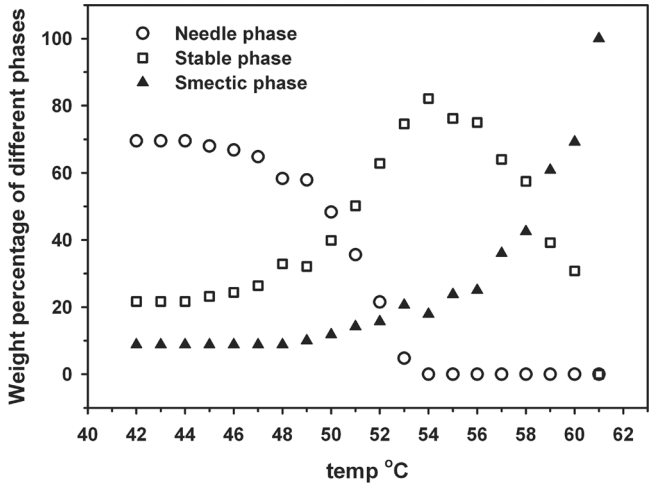

FIGURE 4 Evolution of the composition of 8OCB sample when heated at rate of 2°C/min. The heating was preceded by a process cooling from 90°C at a rate of 5°C/min and a holding at 30°C for 10 minutes.

above 54°C, the stable crystal and the smectic phase survived, and the content change was solely resulted from the melting of the former and transforming into the latter. We are more interested in the relative portion that the needle crystal transformed into the other two phases in region II. The figure points out that the smectic phase experienced a 9% gain in fraction in contrast to a 60% gain of the stable crystal in this region. This is reasonable since the transformation of the meta stable needle crystal into the stable crystal is energetically favorable than that into the smectic phase. Hori and Wu [4] showed by a DSC study of 8OCB single crystals of the needle form that depending on the rate of heating there are two modes for the transformation of the needle crystal: at a high heating rate, the crystal could directly melt into the smectic phase without intermediating through the stable phase, while a slow heating process could result in a transformation of the needle form into the stable phase without any portion of smectic phase formation. Our results obviously followed a different mode of transformation allowing the needle crystals to transform in parallel into the smectic phase and the stable crystal at different portions. The difference in the mode of transformation could be attributed to the presence of the smectic phase and the stable crystal at the beginning of the heating process, while the needle crystal assuming a superlattice could be another cause for the difference. We did not exclude

the possibility that the difference could be attributed to the effect of heating rate since our heating rate sat between the rates of their experiments.

The evolution of SAXS pattern in the heating process at a rate of 5°C/min for an 8OCB sample that cooled from isotropic liquid state and stored at room temperature for weeks is shown in Fig. 5. At temperature below 51°C, the SAXS patterns of the sample were essentially the same. One can see a broad peak spreading from $q = 1.96$ to $2.28\,\mathrm{nm}^{-1}$ accompanied with a small peak centered at $q = 2.78\,\mathrm{nm}^{-1}$. The broad peak was a composite of peaks because it trailed a tail, and a peak at $q = 2.14\,\mathrm{nm}^{-1}$ emerged from the broad peak and grew with rising temperature as temperature exceeded 51°C. A careful inspection could find that simultaneously two other peaks at 2.58 and $2.85\,\mathrm{nm}^{-1}$ emerged and started to grow. This set of peaks has been related to the stable crystal previously and hence the SAXS patterns demonstrated that the stable crystal, which was initially present as a minor component, started to increase its volume fraction after temperature exceeded 51°C and, finally, disappeared at a temperature between 66 and 69°C. The temperature at which the stable crystal completely disappeared is at least 5°C higher than that observed in the 2°C/min heating rate experiment. This difference could result from difference in heating rate. It can be seen from the figure that the smectic peak at $q = 1.98\,\mathrm{nm}^{-1}$ became noticeable at 59°C, and it

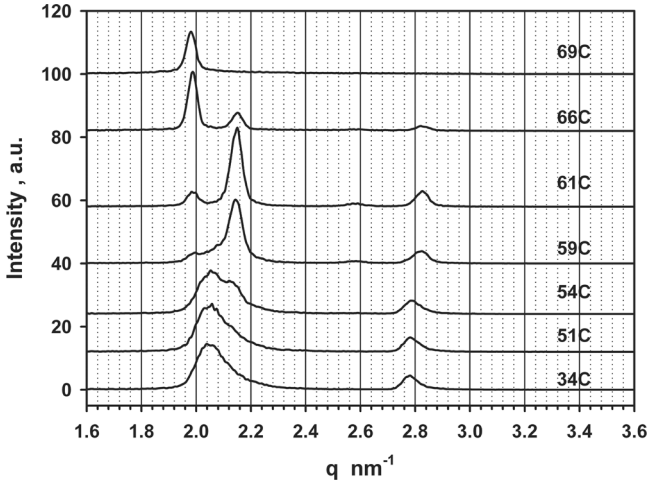

FIGURE 5 Selected SAXS patterns of 8OCB sample when heated at a rate of 5°C/min. The sample was prepared by cooling from isotropic melt to room temperature and stored at the temperature for weeks.

continuously grew and became the sole survivor at 69°C. Thus, the smectic phase should also be present at the beginning as a minor component and continuously increased its portion as temperature increased. Through the analysis above, the broad peak shown in SAXS patterns at low temperatures is now confirmed to be a composite peak, which consisted of at least two peaks: the smectic peak at $1.98\,nm^{-1}$ and another peak at $q = 2.14\,nm^{-1}$ related to the stable crystal. We tried to de-convolute the broad peak into Gaussian peaks centered at 1.98 and $2.14\,nm^{-1}$ but never succeeded unless an additional Gaussian peak at $2.06\,nm^{-1}$ was introduced. In fact, the peak at $2.06\,nm^{-1}$ is easy to perceive from the SAXS pattern at 54°C. The peak at $2.06\,nm^{-1}$ is strongly correlated to the peak at $2.78\,nm^{-1}$ because after the de-convolution of the composite peaks at lower temperatures it was found that the former weakened synchronically with the latter. Thus we conclude that the peaks at 2.06 and $2.78\,nm^{-1}$ related to another form of crystal. Based on the known sequence of the phase change upon heating processes such as those in DSC experiments, this form of crystal could be the parallelepiped crystal whose lattice constants were reported by Hori et al. [2]. Unfortunately, we could not find any prediction from the lattice constants to match the locations of these two peaks. Another form of 8OCB polymorphism was also reported with a different set of lattice parameters [5] which also denied our peaks in SAXS results. Hori et al. [1] identified an intermediate phase of 7OCB by powder XRD investigation. It has a great chance that these two peaks also belonged to a new phase that is similar to the intermediate phase of 7OCB. The reasons are: first, 8OCB resembles to 7OCB greatly in both molecular structure and crystalline behavior, which is evidenced by their isomorphism [1]; second, the location of the diffraction peaks of the intermediate phase of 7OCB are very close to these two peaks of 8OCB. Our calculation based on the data from Hori et al. shows that the peaks of 7OCB locate at the diffraction angles corresponding to 28.6 and 21.5 Å, while the locations of the diffraction peaks for the new phase of 8OCB, 2.06 and $2.78\,nm^{-1}$, correspond to d spacings of 30.5 and 22.6 Å. It is reasonable that the dimensions of 8OCB unit cell are slightly larger if these two crystals share a common crystalline structure; third, the intermediate phase of 7OCB was found in the sample that stored at room temperature for weeks [1], which exactly matched storage condition for the sample of 8OCB we studied. It is worth mentioning that the needle crystal had never appeared during the heating process since its signature of peak at $q = 3.16\,nm^{-1}$ was never detected throughout the process. This is reasonable since the crystal is unstable in a long time period of storage.

Similarly, the transformations between crystalline phases and the smectic phase in heating the aged sample are shown in Fig. 6. It is seen that the transformation of the new phase into the stable crystal started at 46°C and continued at a slow pace until 54°C was reached. Formation of the smectic phase was not observed during the period since the content of the liquid crystalline phase did not increase. When temperature exceeded 54°C, the amount of the new phase decreased at a much higher rate to rapidly enhance the content of the stable crystal, and the fraction of the smectic phase started to increase at a rather low rate. It was until the temperature reached 60°C the content of the the stable crystal displayed its highest, and the smectic phase rapidly became dominant. The evolution of the contents of the three different components indicated that at low temperatures the new phase was incapable of directly transforming into the smectic phase at the heating rate and only when temperature was above 54°C, the new phase transformed into the stable crystal and into the smectic phase could occur in parallel. The transformation of the new phase crystal into the stable crystal and the coexistence of the two phases at room temperature imply that the new phase is metastable.

With the identification of the new phase, there are four forms of crystals: the stable, the needle, the parallelepiped, and the intermediate form involved in this study. The needle form can be obtained

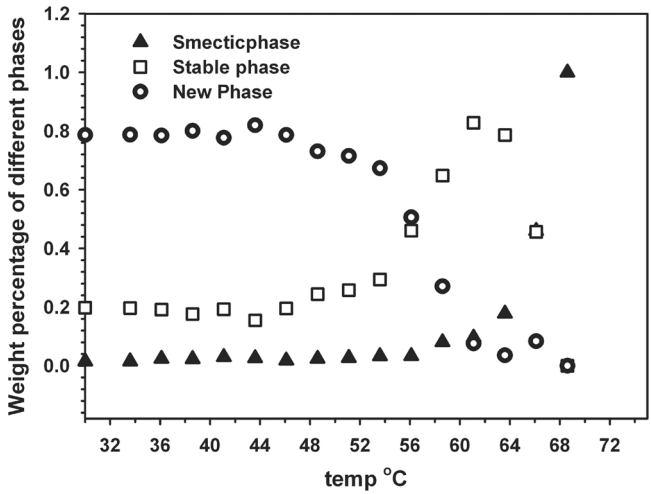

FIGURE 6 Evolution of the composition of 8OCB sample when heated at a rate of 5°C/min. The sample was prepared by cooling from isotropic melt to room temperature and stored at the temperature for weeks.

accompanied with the stable phase from the crystallization of isotropic melt of 8OCB and after a few weeks of storage at room temperature the crystal mixture that obtained from crystallization process transforms into a mixture of the new and the stable phase. This implies that at room temperature the new phase could be obtained from the transformation of the needle phase though at a rather sluggish rate. Upon heating the needle phase, it only transforms into the stable and smectic phase, and no sign of transformation into the new phase occurs. If the needle phase were able to transform into the new phase upon heating, the transformation is expected to happen at the temperature between the melting points of the needle and the stable crystal. Our DSC and SAX experiment did not detect the transformation within the temperature range. This is probable since both phases are metastable, and the probability to observe the transformation between the two metastable phases is much lower than that for transformation from a metastable phase to a stable phase from the perspective of stability.

The phase relationship from the crystalline polymorphs of 7OCB is different from that of 8OCB. The former relationship allows the transformation of the needle phase into the intermediate phase, while upon heating the needle phase of 8OCB does not transform into the new phase, the counter part of the intermediate phase of 7OCB. The difference in the phase relationship of the two mesogenic materials could possibly be attributed to the nematogenic nature of 7OCB and the smectogenic nature of 8OCB, and the even–odd effect of the alkyl group could be also responsible.

4. CONCLUSION

One stable form of crystal, a metastable form and a new phase of 8OCB, have been identified by SAXS. A sample of 8OCB could be a mixture of crystallites of different crystalline forms and the smectic phase in different portions depending on its thermal history. Cooling an isotropic sample at a rate of 5°C/M produced a mixture of smectic liquid and crystallites of the stable and the needle form. The mixture evolved into a composite of smectic liquid and crystallines of the stable form and a new phase after storing at room temperature for weeks. Our time-resolved SAXS study revealed that when the former mixture was heated at rate of 2°C/min, the transformation from the needle crystal into the stable crystal and that into the smectic phase occurred in parallel. When the latter mixture was heated at a rate of 5°C/min, at low temperatures the sole transformation occurring was that the new phase transformed into the stable crystal, and above

54°C the new phase was able to transform into the stable crystal, and the smectic phase in parallel. The SAXS results were slightly inconsistent with the reported crystalline structures of the needle form. The inconsistency could result from the presence of the stable crystal and the smectic phase which induce distortion to the lattice of the needle crystal.

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