



# Smectic liquid crystal Schlieren texture in rapidly cooled poly(butylene naphthalate)

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## ABSTRACT

The morphology of partially crystalline/ordered poly(butylene naphthalate) (PBN) forming on cooling the melt has been analyzed by polarized-light optical microscopy (POM) and microfocus-beam X-ray diffraction (XRD). Crystallization at rather low supercooling of the melt, at temperatures higher than about 200 °C, leads to slow and irregular spherulitic growth of  $\beta'$ -crystals, with spherulites not showing a distinct Maltese cross in POM. At temperatures between approximately 200 and 160 °C, the melt partially converts directly to  $\alpha$ -crystals, and the obtained spherulitic superstructure reveals an increasing nuclei density with decreasing crystallization temperature. At even lower temperature, a liquid crystalline (LC) phase develops. This mesophase may subsequently convert to  $\alpha$ -crystals according to Ostwald's rule of stages. The transition of the LC-phase into  $\alpha$ -crystals is suppressed at temperatures lower than about 120 °C or on cooling faster than about 200–500 K/s. X-ray analysis of PBN liquid crystals formed at well-defined cooling conditions in a fast scanning chip calorimeter revealed smectic periodicity while there is simultaneously observed a distinct Schlieren texture in POM.

## 1. Introduction

Poly(butylene naphthalate) (PBN) is an engineering high-performance polymer which contains a rigid naphthalene ring and flexible methylene sequence in its repeating unit. It is characterized by superior wear and sliding characteristics, hydrolysis and chemical resistance, excellent gas barrier properties, as well as high temperature stability [1,2]. The properties and therefore also potential applications of this polyester are expected to depend on the semicrystalline morphology which typically forms on cooling during melt-processing. However, the effect of the solidification conditions, encompassing the formation of different ordered phases, on the final morphology at ambient temperature, is still not clearly established. Partial ordering of PBN can only be avoided on cooling the melt at rates higher than 6000 K/s to below the glass transition temperature ( $T_g$ ), as recently shown in a study of the vitrification and crystal-nucleation behaviors employing fast scanning chip calorimetry (FSC) [3]. Slower cooling causes the formation of crystals or of a mesophase depending on the specific cooling rate/supercooling of the melt before the phase transition.

In detail, it has been suggested that slow cooling of the melt at rates slower than 10 K/min (0.167 K/s), or crystallization at temperatures higher than about 200 °C, leads to the development of  $\beta'$ -crystals [4–6]. The  $\beta'$ -phase exhibits a triclinic unit cell ( $a_0 = 0.455$  nm,  $b_0 = 0.643$  nm,  $c_0 = 1.531$  nm,  $\alpha = 110.1^\circ$ ,  $\beta = 126.9^\circ$ ,  $\gamma = 100.6^\circ$  [7]) in which the butylene units adopt a nearly all-*trans* chain conformation [8–10], and an equilibrium melting temperature of 281 °C [11]. Morphological information about the  $\beta'$ -crystal polymorph is rare. We are aware of a single study in which it was shown that  $\beta'$ -crystals “grow radially and almost individually from the center” of dendritic spherulites [6], with such morphology attributed to the very slow crystal growth rate. Formation of  $\beta'$ -crystals is increasingly replaced by formation of triclinic  $\alpha$ -crystals ( $a_0 = 0.487$  nm,  $b_0 = 0.622$  nm,  $c_0 = 1.436$  nm,  $\alpha = 110.78^\circ$ ,  $\beta = 121.10^\circ$ ,  $\gamma = 97.93^\circ$  [7]) on increasing the cooling rate to values higher than 0.1 K/min (0.017 K/s), or decreasing the crystallization temperature to below 230 °C. If the cooling rate exceeds 10 K/min (0.167 K/s), or if the crystallization temperature is lower than about 200 °C, then only  $\alpha$ -crystals are forming. The equilibrium melting temperature of the  $\alpha$ -phase is 261 °C,

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that is, about 20 K lower than that of  $\beta'$ -crystals, as was ascribed to the lower packing density [11]. Note that further reports about equilibrium melting temperatures of PBN crystals of 276 °C [6] and 294 °C [12] are available, however, without any assignment to a specific crystal polymorph. The main difference of the crystal structure of the  $\alpha$ -crystals compared to the  $\beta'$ -phase is the conformation of the butylene unit, leading to a shorter fiber identity period (FIP). Growth of  $\alpha$ -crystals is reported being connected with the formation of typical spherulites [6].

If the cooling rate is increased further, as in an early experiment has been achieved by quenching of a 150  $\mu\text{m}$  thin film into ice-water [13], then formation of  $\alpha$ -crystals is suppressed and replaced by the formation of a mesophase. The mesophase has been described being nearly transparent, and possessing a liquid-crystalline (LC) structure with the molecules adopting the same local chain conformation as in  $\alpha$ -crystals. Analysis of the X-ray fiber pattern obtained for a stretched sample led to the conclusion that the PBN mesophase is a smectic-A liquid crystal with a smectic periodicity (layer distance) of 1.43 nm. Importantly, the smectic LC phase has been suggested to exist only below the glass transition temperature of the system, possessing a frozen liquid crystalline structure. As such, the mesophase is more precisely classified as an LC glass [14,15]; heating the LC glass to above its  $T_g$  (65 °C) at a rate of 4 K/min caused transformation into  $\alpha$ -crystals at slightly higher temperature. Later on, the conditions of mesophase formation were further evaluated by FSC and fast X-ray diffraction experiments [16]. It was found that on cooling the melt at rates between 2400 and 24000 K/min (40 and 400 K/s) the mesophase forms as an intermediate transient stage within the path of transformation of the melt into  $\alpha$ -crystals, following Ostwald's rule of stages [17]. This crystallization pathway in which the isotropic melt first transforms into an LC-phase, which undergoes a monotropic transition into a more ordered crystal phase, is not uncommon in aromatic polyesters where the stiff aryl rings act as mesogenic units [18–23]. However, in case of PBN the transition of the LC-phase into crystals is finally suppressed if the cooling rate exceeds 24000 K/min (400 K/s), leading to the above described formation of an LC glass.

For polymers forming a monotropic nematic structure, polarized-light optical microscopy (POM) revealed a fine-grained structure of the LC-phase at the micrometer scale [19–21], modeled as isolated nematic domains embedded in the isotropic phase [22]. Similarly, for a monotropic smectic LC-phase such fine-grained structure was also detected [23]. In the subsequently occurring crystallization process of the nematic and smectic phase, these liquid crystalline structures serve as precursors/nuclei, distinctly increasing the crystallization rate while preserving the initially formed grainy morphology [19–23]. For PBN, however, morphological information about the smectic mesophase is not available yet, which is therefore provided in the present study.

## 2. Experimental

PBN was obtained from Teijin Shoji Europe GmbH in form of additive-free pellets. The intrinsic viscosity of the polymer is 0.92 dL/g and was measured at 30 °C using a mixture of phenol and 1,1,2,2-tetrachloroethane 60:40 w/w.

Differential scanning calorimetry (DSC) was used to obtain crystallization temperatures on cooling at rates lower than about 1 K/s. We employed a Mettler-Toledo DSC 1, operated in conjunction with a Huber TC 100 intracooler, and with the furnace purged using nitrogen gas at a flow rate of 60 mL/min. A sample with a mass of about 5 mg was encapsulated in a 20  $\mu\text{L}$  aluminum pan and heated to 280 °C to obtain a relaxed melt within three minutes holding time, before cooling at different rates. To assure absence of degradation during repeated heating and cooling, reproducibility of crystallization temperatures was checked. Furthermore, to exclude systematic instrumental errors, a Mettler-Toledo DSC 820 was used to confirm the obtained results.

Analysis of non-isothermal crystallization on cooling at rates between 1 and 5000 K/s was done using a Mettler-Toledo FSC connected

to a Huber intracooler TC 100, and using dry nitrogen gas to purge the sample at a flow rate of 40 mL/min. Sensors were conditioned and temperature-corrected before loading with specimens of different mass, using Wacker silicon oil AK 60,000 as contact medium towards the sensor membrane. Samples were prepared from the as-received pellets using a microtome to obtain thin sections with a thickness of less than 20  $\mu\text{m}$  which then were further reduced in their lateral width to about 50–100  $\mu\text{m}$  using a scalpel and a stereomicroscope.

POM was employed to obtain morphological data at the micrometer length scale of PBN of different thermal history. Thin sections with a thickness of about 20  $\mu\text{m}$  were prepared using a SLEE microtome, placed between Plano covers slips and melted at 290 °C on a hot stage. Then the glass-polymer-glass sandwich was either quickly transferred to a second hot stage to allow isothermal crystallization at pre-adjusted target temperatures, or quenched in ice water to achieve fast cooling. The morphology of the samples was then evaluated between crossed polarizers in a Leica DMRX optical microscope in transmission mode, using a Motic CCD camera for imaging.

For the precise analysis of the effect of the rate of cooling the melt of PBN on the formation of the various possible polymorphs, X-ray diffraction (XRD) patterns of FSC samples with a well-defined cooling history have been collected using a SAXSLAB ApS Ganesha 300 XL+ system (Denmark). The samples remained attached to the membrane of the FSC sensor for easy handling and were investigated in transmission mode, using monochromatic Cu K $\alpha$  radiation and a microfocus X-ray beam with a cross-section of 400  $\times$  400  $\mu\text{m}^2$ . For registration of the scattered X-rays, a Pilatus 300K 2D-detector was employed using an exposure time of 30 min. Preferred crystal orientation was not detected, allowing azimuthal averaging of the 2D frames to get XRD curves without loss of information.

The morphology of FSC samples subjected to specific cooling pathways, finally, was evaluated by POM operated in reflection mode, using a Kern OPN 184 microscope equipped with a Leica imaging system.

## 3. Results and discussion

Fig. 1 shows the dependence of the crystallization peak temperature on the cooling rate, together with information about the specific phases developing. Coloring of symbols and lines is used to emphasize formation of  $\beta'$ - and  $\alpha$ -crystals from the isotropic melt (red), of  $\alpha$ -crystals from the LC-phase (blue), and of the LC-phase from the melt (gray/black). Cooling at rates lower than about 0.01 K/s causes crystallization at temperatures higher than about 220 °C and presumably, according to

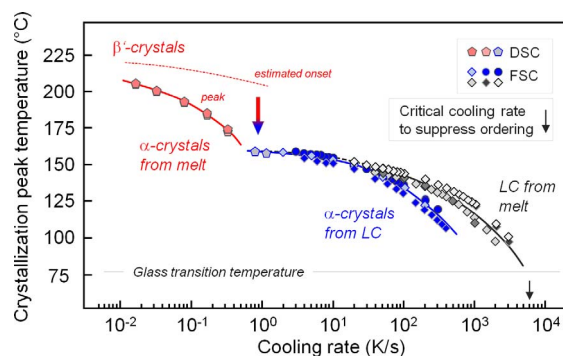


Fig. 1. Crystallization peak temperature of PBN as a function of the cooling rate. Color-coding is used to emphasize formation of  $\beta'$ - and  $\alpha$ -crystals from the isotropic melt (red), of  $\alpha$ -crystals from the LC-phase (blue), and of the LC-phase (gray/black). The vertical black arrow indicates the critical cooling rate above which the isotropic melt vitrifies without prior formation of an ordered phase [3], and the horizontal line approximately represents the glass transition temperature [1]. Note that formation of  $\beta'$ -crystals on very slow cooling, as indicated in the top left corner, was not experimentally proven in this work, but is well described in the literature [4–6]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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