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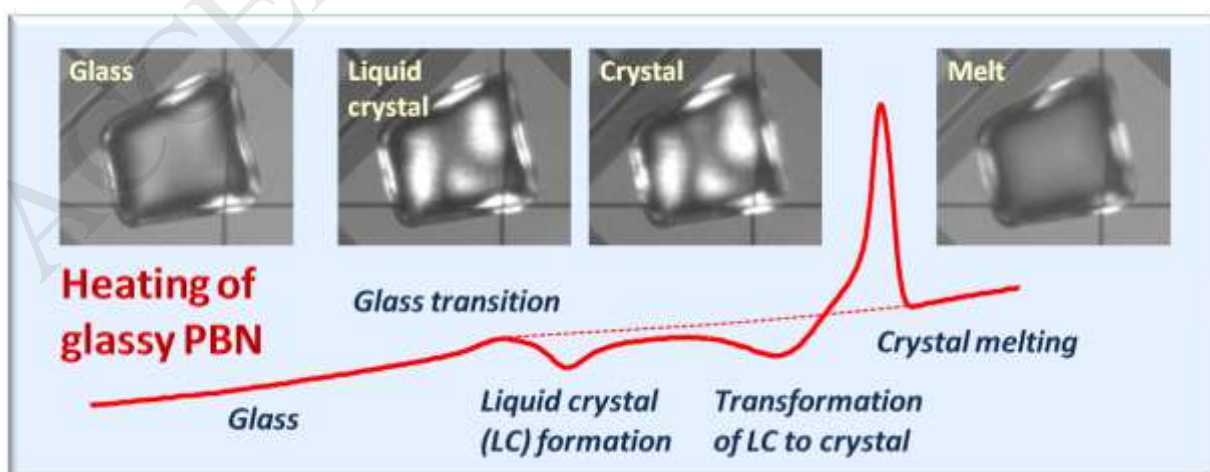
Cold-crystallization of poly(butylene 2,6-naphthalate) following Ostwald's rule of stages

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Graphical abstract



Highlights

- Slow heating of amorphous PBN leads to cold-crystallization following Ostwald's rule of stages.
- Cold-crystallization proceeds via formation of liquid crystals which then transform to crystals.
- The transition of liquid crystals into crystals is not connected with a change of the superstructure.

Abstract

Melt-crystallization of poly (butylene 2,6-naphthalate) (PBN) at temperatures lower than about 160 °C follows Ostwald's rule of stages, leading first to formation of a transient smectic liquid crystalline phase (LC) which then may convert in a second step into crystals, controlled by kinetics. In the present work, the PBN melt was cooled at different rates in a fast scanning chip calorimeter to below the glass transition temperature, to obtain different structural states before analysis of the cold-crystallization behavior on heating. It was found that heating of fully amorphous PBN at 1000 K/s leads to a similar two-step crystallization process as on cooling the quiescent melt, with LC-formation occurring slightly above T_g and their transformation into crystals at their stability limit close to 200 °C. In-situ polarized-light optical microscopy provided information that the transition of the LC-phase into crystals on slow heating is not connected with a change of the micrometer-scale superstructure, as the recently found Schlieren texture remains unchanged.

Keywords: Poly(butylene 2,6-naphthalate); Crystallization; Ostwald's rule of stages; Morphology; Fast scanning chip calorimetry

Poly(butylene 2,6-naphthalate) (PBN) is a linear crystallizable polyester which shows a distinct crystal polymorphism. Cooling the melt slower than about 10 K/min (0.17 K/s) leads to formation of triclinic β' -crystals with an equilibrium melting temperature of 281 °C. If the cooling rate is higher than 0.1 K/min (0.017 K/s), or if crystallization occurs below 230 °C, then β' -crystals are increasingly replaced by triclinic α -crystals with a 20 K

lower equilibrium melting temperature; crystallization at temperatures lower than about 200 °C yields α -crystals only [1–4]. Both the formation of β' - and α -crystals occurs at temperatures higher than about 160 °C directly from the melt. If the melt, however, is supercooled to below about 160 °C, by cooling faster than about 1 to 10 K/s, then the crystallization process involves an intermediate formation of a monotropic liquid crystalline (LC) mesophase [5–8], following Ostwald's rule of stages [9]. The thermodynamics behind the one- and two-step crystallization process of PBN at temperatures higher and lower than about 160 °C, respectively, is schematically illustrated in Figure 1 which shows the temperature-dependence of Gibbs enthalpy of the melt (black), of the monotropic mesophase (blue) and of the crystal phase (red). At temperatures above the stability-limit of the mesophase, indicated with the blue circle, crystallization occurs directly from the melt while at lower temperatures formation of crystals proceeds according to Ostwald's rule of stages via intermediate formation of liquid crystals.

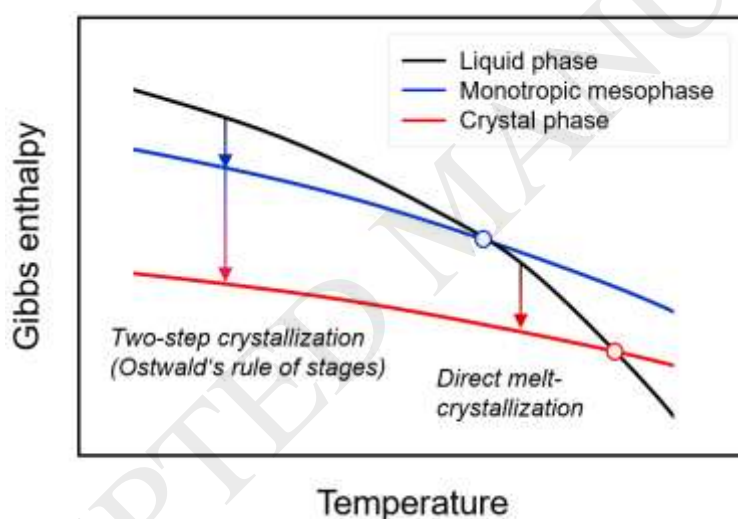


Figure 1: Temperature-dependence of Gibbs enthalpy of the melt (black), of the monotropic liquid-crystalline mesophase (blue), and of the crystal phase (red). Different isothermal crystallization routes below and above the stability limit of the mesophase (blue circle) are indicated with the vertical arrows.

The conversion of the LC phase into crystals, so far, has only been detected between 160 and 130 °C [6, 7]. At temperatures lower than about 130 °C, the transformation of the LC phase into crystals apparently is kinetically suppressed or proceeds slow, leading to vitrification of the LC phase on cooling to below its glass transition temperature $T_{g, LC}$ of about 65 °C [5]. Note that it was reported in the literature that the glass transition temperature of the LC phase is higher than the glass transition temperature T_g of the amorphous phase (42 °C) [5, 8]. A non-equilibrium phase diagram showing the cooling-rate dependence of temperatures of the various phase transitions of PBN is available in the literature (see Figure 1 in [7]).

The formation of the LC phase in PBN likely is related to the presence of the naphthalene group which is considered mesogenic [10]. The LC phase in PBN is monotropic and is characterized by a smectic periodicity with a layer distance of 1.43 nm [5], being approximately the length of the chain repeat unit, and by appearance of a distinct Schlieren texture at the micrometer length scale [7]. Analysis of the bulk enthalpy of its formation showed that the transition of the melt into the LC phase contributes to only about 20% to the total enthalpy of crystallization, confirming its smectic nature since in case of a nematic phase the enthalpy of formation would be much lower [11, 12].

The formation of crystals and LC phase is fully suppressed on cooling the melt to below ~~the glass transition temperature of the amorphous phase (T_g)~~ at 6000 K/s, or faster [8]. Moreover, it was found that a cooling rate higher than 30,000 K/s is needed to avoid the development of homogeneous nuclei. Both LC-phase formation and crystallization on heating the glass to above T_g is hindered if the heating rate is higher than 7000 K/s, even if nuclei are present. A detailed analysis of structural changes on heating PBN of different initial structure, from fully amorphous to samples containing mainly LC phase and samples containing mainly crystals, was performed at a heating rate of 2000 K/s. In case of initially fully amorphous PBN, heating at 2000 K/s allowed LC-phase formation at around 135 °C followed by its disordering at about 180 °C, without prior transformation into crystals. Suppression of the transition of LC phase into crystals on heating faster than 1000 K/s was then confirmed in an independent study, which focused on analyses of the enthalpy of LC-phase formation and the LC-disordering temperature in isothermally ordered PBN [12].

In the present work we report about the cold-ordering and cold-crystallization behaviors of PBN of different initial structure, controlled by variation of the rate of prior cooling the melt. In contrast to previous work, the analysis was done using a lower rate of 1000 K/s,

purposely applied to possibly detect conversion of the LC phase, formed after devitrification of the glass, into crystals and with that validating of Ostwald's rule of stages in a heating experiment. In addition, we attempted gaining information about the morphology of the LC phase as well as of the semicrystalline structure forming in sequence on heating the glass.

Due to the high cooling rates needed to obtain glassy PBN, we employed a fast scanning chip calorimeter (FSC) Flash DSC 1 (Mettler-Toledo, Switzerland) for preparation of PBN of different structure and for their subsequent calorimetric analysis during heating. General information about the instrument design and performance is provided elsewhere [13, 14]. In the specific setup used for fast cooling experiments in this work, the FSC was connected to a Huber intracooler TC 100, and the sample environment was purged with dry nitrogen gas at a flow rate of 40 mL/min. Samples were prepared using a microtome to obtain thin sections with a thickness of less than 20 μm which then were further reduced in their lateral width to about 50–100 μm using a scalpel and a stereomicroscope. Before loading the specimens onto the heatable area of the chip membrane, sensors were conditioned and temperature-corrected according the instrument specification.

A slow-cooling experiment was conducted with a conventional differential scanning calorimeter DSC 820 from Mettler-Toledo. Temperature-resolved analysis of the morphology of amorphous PBN and PBN containing the LC phase at room temperature was performed by polarized-light optical microscopy (POM), using an external chip sample holder connected to the FSC main device, by wire-extension of the electrical pin-connectors of the main device (Functional Materials Rostock e.V., Germany). In that case, the instrument was operated without using the intracooler, with the sensor-support temperature being room temperature. The external sample holder was placed onto the sample stage of a Kern OPN-184 reflection mode POM with the PBN sample monitored between crossed polarizers while subjected to specific heating and cooling steps. Note that despite an external cooling device was not used, it was possible to linearly cool samples at 1000 K/s to temperatures below T_g ; to obtain amorphous PBN at ambient temperature a ballistic rapid-cooling experiments was designed allowing cooling in the crystallization-relevant temperature range at a rate >5000 K/s. Video recording was done with an Imaging-Source DFK 33UX252 camera, used in conjunction with the IC Capture software. PBN was synthesized by a two-stage polycondensation reaction, starting from 2,6-dimethylnaphthalate and 1,4-butanediol, using titanium tetrabutoxide as a catalysts, with

details of the synthesis published elsewhere [15]. The number-average molar mass and polydispersity were 23 kDa and 2.13, respectively, and the intrinsic viscosity of 0.94 dL/g was determined at 30 °C using a mixture of phenol and 1,1,2,2-tetrachloroethane 60:40 w/w.

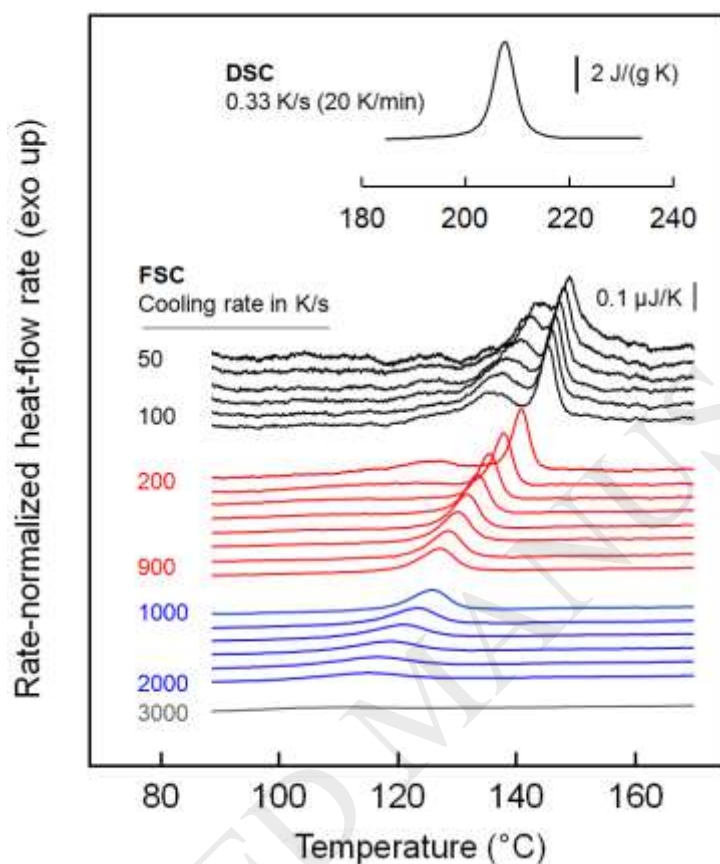


Figure 2: Rate-normalized FSC cooling curves, recorded at different rates between 50 K/s (top curve) and 3000 K/s (bottom curve). The inset at the top shows a DSC cooling scan, recorded at 0.33 K/s (20 K/min).

Non-isothermal cold-ordering/-crystallization experiments were performed on PBN samples of largely different initial structure, with the latter obtained by variation of the cooling conditions. Figure 2 is a plot of FSC cooling curves recorded at rates between 50 and 3000 K/s and of a DSC scan obtained during cooling at 0.33 K/s (20 K/min) (inset at the top of the Figure). As expected, slow cooling at 0.33 K/s is connected with a single crystallization event at a temperature higher than 200 °C, that is, with direct conversion of the melt into crystals, confirmed by XRD data in former work [7]. Observation of direct conversion of the melt into crystals is maintained up to cooling rates of about 10 K/s, however, if cooling is performed at rates between 50 and about 200 K/s then a two-step crystallization process is detected, with the high- and low-temperature peaks attributed to

formation of LC phase and transformation of the LC phase into crystals, respectively. As in case of an earlier investigated different PBN-grade [6, 7], cooling faster than about 100 K/s leads to partial suppression of the transformation of the LC phase into crystals, and on cooling faster than 300–400 K/s it cannot be detected anymore. Then only a single ordering peak is seen which diminishes with increasing cooling rate, to be almost completely absent on cooling at 3000 K/s. As such, according to Figure 2, it is possible to obtain fully amorphous PBN (after cooling at 3000 K/s, or faster), and PBN containing different amounts of LC phase (after cooling at rates between about 400 and 2000 K/s), and PBN containing crystals (after cooling at rates lower than about 300 K/s). Naturally, within certain cooling-rate ranges, LC phase and crystals co-exist, together with amorphous structure.

Without in-between annealing, the samples of different cooling history were immediately re-heated at a rate of 1000 K/s, in order to possibly detect cold-ordering/-crystallization events. The corresponding FSC heating curves are shown in Figure 3, with the color-coding of data being in accord with that of the cooling curves of Figure 2, for easy assignment; the bold curves in each of the four groups of curves refer to the respective highest cooling rate in prior solidification. Most important is the observation of two exothermic peaks in the heating curves of initially fully or almost fully amorphous samples (lower three curves, obtained on samples solidified at 3000, 4000, and 5000 K/s). Immediately after devitrification of the amorphous glass, the melt transforms into the LC phase at around 120 °C and then, on further heating, the LC phase crystallizes well above 160 °C. While the temperature of LC-phase formation seems independent on the prior cooling rate, the peak area decreases with decreases cooling rate. Supported by close inspection of the cooling scan obtained on solidifying the sample at 3000 K/s (bottom curve in Figure 2), it is obvious that small amount of LC phase formed already on cooling, leading then to a smaller cold-ordering peak on subsequent heating. In contrast, the crystallization peak shifts with decreasing rate of solidification to lower temperature which translates to faster crystallization if the LC phase was partially formed already during prior cooling, perhaps due to generation of first nucleation sites for the transition of the LC phase into crystals during the longer time of its presence. Both trends are observed also for samples cooled between 1000 and 2000 K/s (blue curves). In this cooling-rate range, with decreasing cooling rate LC-phase cold-ordering diminishes due to LC-phase formation already during cooling, leading to a shift of the temperature of cold-crystallization to lower temperature; again, the latter observation is believed related to the formation of nucleation

sites for the specific phase transformation, being kinetically controlled and being therefore enhanced on lowering the cooling rate. With decreasing rate of cooling between 900 and 200 K/s, transformation of the LC phase into crystals is increasingly permitted on cooling. In the heating scans of Figure 3 (red curves), the area of the cold-crystallization peaks decreases though there is no further shift to lower temperatures. Obviously, LC-phase formation during cooling is not anymore a function of the cooling rate and completes during cooling.

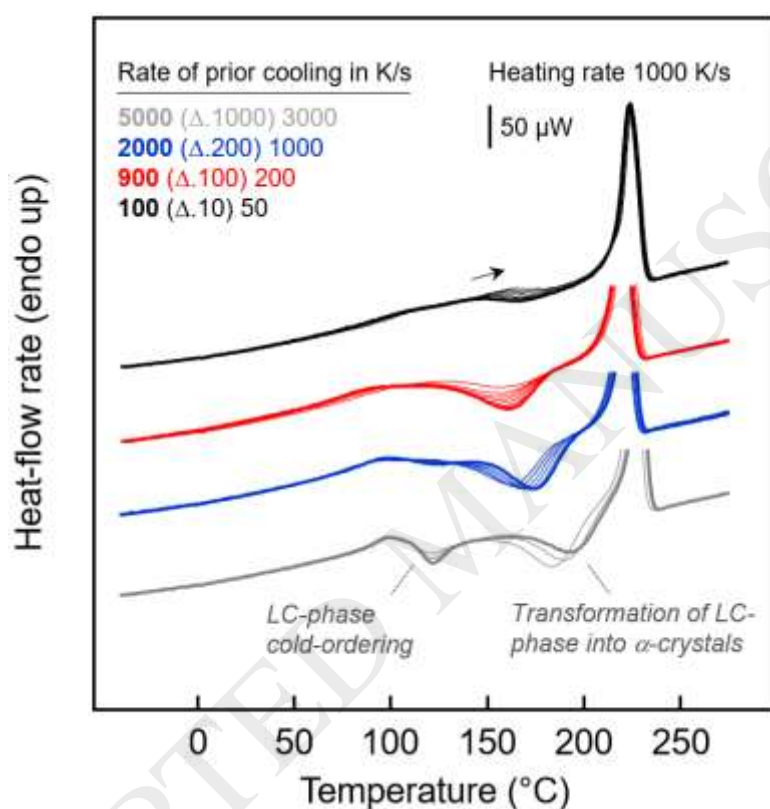


Figure 3: FSC heating curves PBN solidified on cooling at different rates (see Figure 2), recorded at a rate of 1000 K/s. Color-coding of curves is in accord with that of the cooling curves of Figure 2.

Finally, cooling at rates between 100 and 50 K/s allows complete reorganization of the LC phase into crystals on cooling which explains the absence of a large exothermic peak on subsequent heating. With decreasing cooling rate the transition of the LC phase into crystals occurs at higher temperature, producing crystals of higher stability. Accordingly there is observed a slight shift of the onset of melting toward higher temperature in the heating scans (see arrow), with the melting event masked by classical crystal reorganization, followed by melting at around 220 °C. Susceptibility of PBN crystals to reorganization on heating, however, is also confirmed with the observation of melting at a

temperature which is almost independent on the thermal history. Regardless the initial state of structure of the PBN samples, the final melting temperature is about constant which is a strong indication of a process of melting of unstable crystals, melt-recrystallization, and remelting, with its extent controlled by the heating rate [16–19].

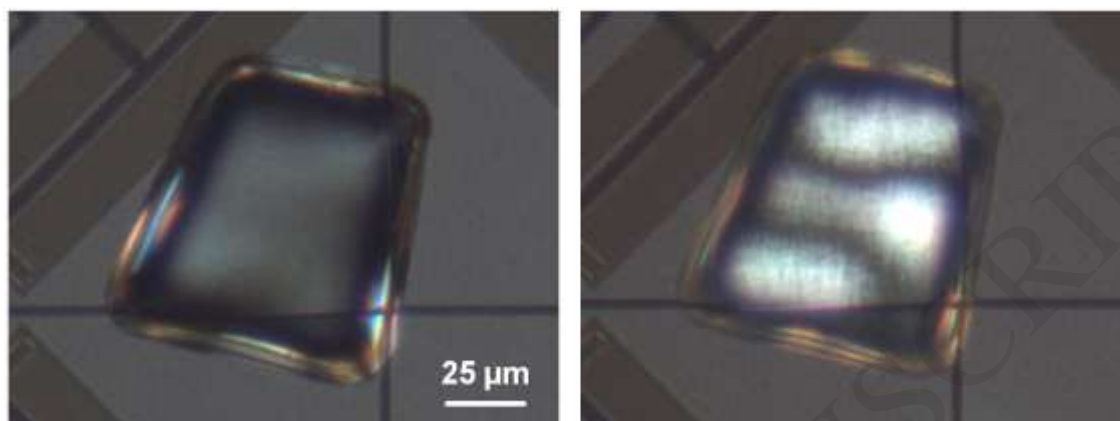


Figure 4: POM micrographs of PBN placed on an FSC chip sensor after rapid cooling to below T_g faster than 5000 K/s (left) and after cooling at 1000 K/s (right).

Analysis of the semicrystalline morphology of numerous polymers revealed that transformation of ordered phases of low metastability (conformationally disordered crystals; small crystals) into crystals of higher stability during heating occurs at a local length scale without prior global melting [20–23]. In such case the density of nuclei evident on initial formation of the mesophase is preserved, and the superstructure of the ordered domains/crystals within the amorphous surrounding is unchanged. While for melt-crystallization of PBN at cooling rates which enforce intermediate formation of the LC-phase the absence of formation spherulites and conservation of the specific orientation of birefringent crystals, as predefined by the Schlieren texture of the LC phase, has been confirmed (see bottom left image of Figure 6 in [7]), in this work an in-situ POM analysis of structure evolution on heating initially fully amorphous PBN and PBN containing mainly LC phase has been performed. These samples were prepared in the FSC, which is required to subject the samples to the needed high cooling rates. Figure 4 shows the POM structure of PBN which was cooled at a rate higher than 5000 K/s (left image) and at a rate of 1000 K/s (right image) to below T_g . The left image confirms that on cooling ordering was almost completely suppressed and that the sample is nearly amorphous. However, careful inspection of the image reveals a slight haze or brightening, indicating that orientation of mesogens was not fully suppressed, requiring faster cooling and more

advanced instrumentation. The right image reveals the expected Schlieren texture of the LC phase, with the corresponding FSC cooling scan in Figure 2 proving that crystallization of the LC phase was suppressed on cooling at 1000 K/s since showing only a single ordering peak.

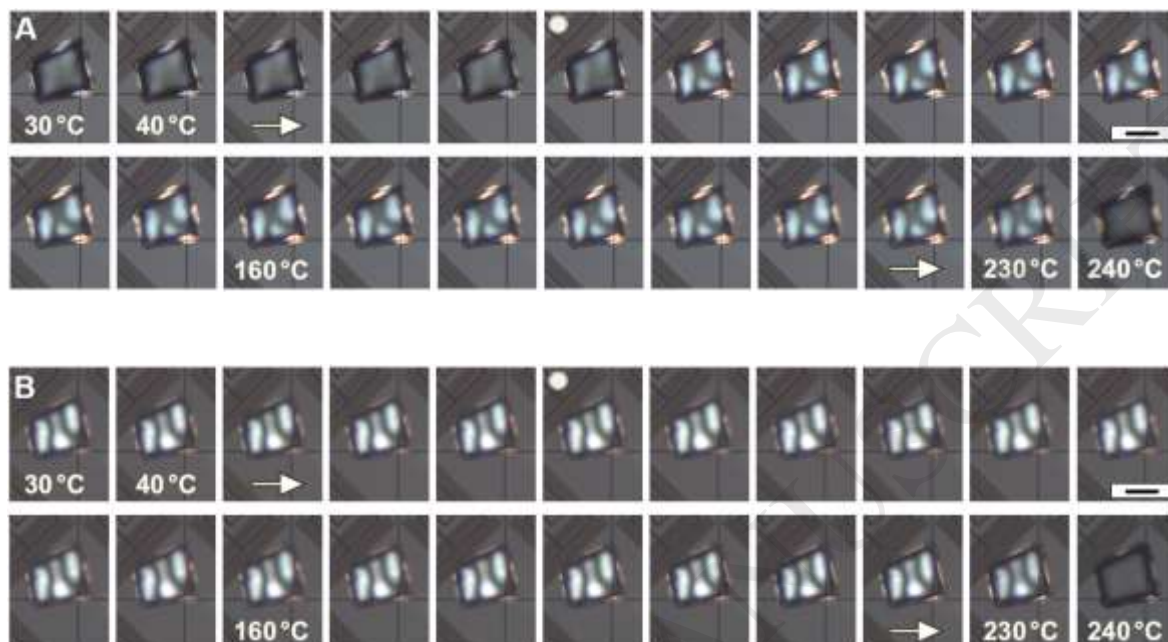


Figure 5: Sets of POM micrographs of (A) initially almost fully amorphous/isotropic PBN and (B) of PBN containing LC phase at ambient temperature. The images were captured on heating at a rate of 1 K/s from 30 °C (left image in upper row) to 240 °C (right image in lower row). Micrographs shown were taken every 10 s, that is, after an increase of the temperature by 10 K. The circles refer to a temperature around T_g , and the scale bars represent a distance of 50 μm .

The samples of Figure 4 were then slowly heated at a rate of 1 K/s in the FSC while monitoring the POM-structure. Selected images of the initially almost fully isotropic sample and the sample containing the LC phase are shown in Figures 5 (A) and 5 (B), respectively. The set of images in each Figure needs to be read line-wise, with begin and end of the heating experiment represented with the left image in the upper row (taken at 30 °C) and the right image in the lower row (taken at 240 °C), respectively; micrographs shown were taken every 10 s, that is, after an increase of the temperature by 10 K. The images of Figure 5 (A) reveal that amorphous PBN begins to form the LC phase immediately after devitrification at T_g . The image containing the circle in the upper left corner was captured at 80 °C, that is, at a temperature around or slightly above T_g , showing first signs of brightening; latest at 90 °C the LC-phase-characteristic texture is clearly visible. According to the lower three FSC scans of Figure 3 (gray curves), though

measured at a heating rate of 1000 K/s, the LC phase transforms to α -crystals at around 160 °C, which then further reorganize and increase their stability within the available time-frame controlled by the heating rate. However, the POM-structure is not affected by both crystallization and subsequent crystal reorganization as the texture initially formed at 80–90 °C is preserved until final melting slightly above 230 °C. Similarly, the images of Figure 5 (B) reveal that cold-crystallization of the LC-phase, which formed during cooling of the melt, has no effect on the POM-structure. When heating the LC phase at rates between 1000 and 2000 K/s then cold-crystallization occurred at around 160 °C (see blue curves in Figure 3), however, the images obtained around this temperature in the bottom row of Figure 5 (B) remain unchanged and keep the Schlieren texture until final melting slightly above 230 °C.

In summary, the performed study of the cold-crystallization behavior of PBN permits the following conclusions:

(i) Heating of glassy PBN at a rate of 1000 K/s allows formation of LC phase slightly above T_g at about 120 °C and its transformation to crystals between 150 and 200 °C. In prior work it was furthermore shown that formation of the LC phase and its transformation into crystals is suppressed on heating faster than 7000 and 1000 K/s, respectively [7, 8]. At the cold-crystallization conditions applied here, Ostwald's rule of stages is valid. It is assumed that ultra-fast heating (>7000 K/s) of amorphous PBN to temperatures higher than about 160 °C, followed by isothermal annealing below the equilibrium melting temperature is connected with direct transformation of the melt into crystals, though evidence is lacking.

(ii) Cold-ordering of initially glassy PBN, yielding the LC phase, leads to observation of the same Schlieren texture as on cooling. The transformation of the LC phase into crystals has no effect on the 10 μm scale (macroscopic) birefringence pattern in POM. It may be assumed that the transition of the LC phase into crystals must only involve local molecular rearrangements if Ostwald's rule of stages is valid, that is, a transition path via the melt, as in classical crystal reorganization processes, may be excluded in the two-stage crystallization process (as in case of the Form II/Form I transition in isotactic polybutene-1 [24, 25]). It can therefore be anticipated that the transition of the LC phase into crystals only involves very local rearrangements of structural motifs at a length scale of neighbored chain segments, invisible in POM.

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