Thermochimica Acta 670 (2018) 71–75

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short communication

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

René Androsch[a,*], Michelina Soccio[b], Nadia Lotti[b], Dario Cavallo[c], Christoph Schick[d,e]

[a] Interdisciplinary Center for Transfer-oriented Research in Natural Sciences (IWE TFN), Martin Luther University Halle-Wittenberg, 06099 Halle/Saale, Germany
[b] Civil, Chemical, Environmental and Materials Engineering Department, University of Bologna, Via Terracini 28, 40131 Bologna, Italy
[c] Department of Chemistry and Industrial Chemistry, University of Genova, Via Dodecaneso 31, 16146 Genova, Italy
[d] University of Rostock, Institute of Physics and Competence Center CALOR, Albert-Einstein-Str. 23–24, 18059 Rostock, Germany
[e] Kazan Federal University, 18 Kremlyovskaya Street, Kazan 420008, Russian Federation

ARTICLE INFO

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

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.

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 Fig. 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.

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 Fig. 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

* Corresponding author.
E-mail address: rene.androsch@iw.uni-halle.de (R. Androsch).

https://doi.org/10.1016/j.tca.2018.10.015
Received 19 August 2018; Received in revised form 8 October 2018; Accepted 13 October 2018
Available online 15 October 2018