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Morphology of α-crystals of poly (butylene 2,6-naphthalate) crystallized via a liquid crystalline mesophase according to Ostwald's rule of stages

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ABSTRACT

Poly(butylene 2,6-naphthalate) (PBN) is a crystallizable aromatic polyester and develops different crystal polymorphs as a function of the crystallization conditions. High-temperature crystallization above about 200 °C yields β′-crystals while α-crystals develop between about 160 and 200 °C, both forming directly from the melt. At lower temperature, crystallization follows Ostwald's rule of stages, with the melt first transforming into a smectic liquid crystalline structure, which then converts into α-crystals. Information about the morphology of the liquid crystalline mesophase at the nanometer-length scale and of α-crystals, formed directly from the melt or from the liquid crystalline mesophase, are not available yet, and is therefore analyzed in the present study using atomic force microscopy (AFM). Direct transformation of the melt into α-crystals proceeds via spherulitic crystal growth. AFM reveals formation of laterally extended lamellae with a thickness of 10–15 nm. The smectic liquid crystalline mesophase, isolated by quenching before its transformation into α-crystals, appears as a close arrangement of clusters with a characteristic spacing of around 10 nm. The overall morphology is preserved on transformation of the mesophase into α-crystals supporting the notion that the mesophase converts directly, that is, within a solid-solid phase transition into α-crystals without intermediate melting, confirming a crystallization pathway according Ostwald's rule of stages.

1. Introduction

Poly(butylene 2,6-naphthalate) (PBN) is a crystallizable high-performance linear-chain polyester of great industrial interest, attributed to its good mechanical properties, excellent thermal and chemical resistance, and outstanding barrier properties [1]. The PBN chain repeat unit contains a rigid naphthalene ring and a flexible butylene group, allowing for rather fast crystallization on supercooling the melt to below the equilibrium melting temperature ($T_{m,0}$) [2,3]. Suppression of crystallization/ordering processes requires cooling the melt to below the glass transition temperature T_g of 78 °C [1] at rates higher than 6.000 K/s [4], which is distinctly faster than observed for many other crystallizable polymers [5]. The maximum crystallinity of PBN is around 30–40%, considering frequently reported values of melting enthalpies around 40–50 J/g [2,3,6] and a bulk specific enthalpy of melting of 122 J/g (33 kJ/mol) [6,7], with this rather low value also attributable to the low chain mobility within the crystalline phase [8]. In addition, PBN is polymorphic, that is, as a function of the conditions of crystallization different crystal polymorphs develop [9]. At a glance, crystallization at temperatures higher than about 160 °C involves direct conversion of the melt into the final crystal structure while crystallization at lower temperatures proceeds via intermediate formation of a liquid crystalline (LC) mesophase according to Ostwald's rule of stages. Ostwald's rule of stages implies that "*in the course of transformation of an unstable (or meta-stable) state into a stable one the system does not go directly to the most stable conformation (corresponding to the modification with the lowest free energy) but prefers to reach intermediate stages (corresponding to other possible meta-stable modifications) having the closest free energy difference to the initial state*" [10–14]. In the specific case of PBN, at favorable conditions, that is, at temperatures lower than 160 °C, the unstable melt transfers first to a transient or metastable (monotropic) mesophase which only then transfers into stable α-crystals. The mesophase can be

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