ABSTRACT

Using Tapping-Mode atomic force microscopy, we studied crystallization of polymers in confined cylindrical geometries of micro-phase separated asymmetric diblock copolymers, deposited in thin films onto solid substrates. We observed that crystallization occurs separately and independently in each cylinder of the mesophase pattern. We followed the kinetics of the crystallization process with time and found an influence of the lateral size of the cylindrical morphology (determined by the weight fraction of the crystallisable block) on the rate of crystallization. The present data are compared to previous results on spherical mesophase patterns. The growth rate within one single cylinder was found to be not necessarily constant. Depending on the amount of crystallized material and the molecular weight, the structural relaxations of the crystals can have very strong influence on the amorphous matrix and can even lead to the destruction of the mesophase pattern, allowing for break-out crystallization. As a consequence of break-out crystallization, crystallization kinetics changed considerably since the crystal growth is not limited anymore to the confinement imposed by the cylinders.

AFM phase images of hydrogenated poly(butadiene-b-ethylene oxide) (PB₇₀-b-PEO), with a molecular weight of the blocks of 3700 and 1100 g/mol, respectively, corresponding to a PEO weight fraction of 28%. The size is 1 x 1 µm². These samples are crystallized for different intervals of time at –17 °C: (A) - 2 min, (B) - 20 min,(C) – 40 min and (D) – 60 min. The average overall amount of crystallized PEO cylinders is about 5 %, 20 %, 60 % and 80 %, respectively.