Semi-crystalline polymers typically consist of crystalline and amorphous domains with dimensions in the nanometer range, which form lamellar stacks in a spherulitic superstructure. The final properties of such a polymer depend on the volume fraction of the crystalline domains as well as on their size and structure. In addition, the linkage between the crystals and the amorphous interlamellar regions is an important factor. In fact, all these effects are correlated. For example, changes on a length scale of 0.1 nm due to a crystalline transition may induce a morphological reorganization on a length scale of nanometers. Small angle x-ray scattering (SAXS) is well suited to investigate this kind of phenomena. From SAXS one detects crystalline transitions from any discontinuity in the invariant Q and in the morphological parameters extracted [1-5]. Here we employ simultaneous SAXS and WAXS to explore the crystalline transitions and the corresponding morphological changes in nylon 12. Time resolved SAXS-WAXS measurements were made at EMBL-beamline X33 of HASYLAB (DESY, Hamburg) on the temperature dependence of crystalline structure and morphology of nylon 12. The objective is to investigate the influence of the crystalline structures and their mutual transitions on the morphology.

Fig. 1a and b display the WAXS and the SAXS profiles of sample I as a function of temperature, starting from the α’-phase after crystallization at 175 °C. The d-spacing and crystalline thickness, obtained with Gaussians peak fitting and one-dimensional density correlation function respectively, are shown in Fig. 2 a and b respectively.

On the basis of our WAXS measurements a simple picture of the phase diagram of nylon 12 can be given. At high temperatures, nylon 12 is in the α’-phase, which is characterized by two crystalline reflections. The underlying structure still has to be solved. In the temperature range from about 100 to 130 °C, the hexagonally packed γ-form exists with only one reflection. When the temperature is further lowered to 40 °C, two reflections appear again as a result of an anisotropic thermal expansion leading to an orthorhombic structure.

A surface melting and crystallization model is employed to explain the behavior of the crystalline thickness $l_c$ around the transition point (see Fig. 3). As far as the two strong
hydrogen bonds allow, the methylene segment would preferentially remain in the molten state when the temperature is above the equilibrium melting point of PE (about 141 °C). This results in lamellar crystals of nylon 12 with hydrogen bonds at the top and bottom surface. The methylene segment remain as cilia (or methylene brushes) in the interlamellar amorphous layer. When the temperature drops below 141 °C, these methylene brushes can easily be incorporated into the nylon 12 crystalline lattice by epitaxial growth. Meanwhile, the crystalline transition affords the chain mobility for local reorganization.

References