

Lamellar crystal orientation in ultrathin films of aliphatic polyesters

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The synthesis and characterization of new biodegradable polymers is a topic of increasing interest mainly arising from their potential applications in biology and medicine. Among synthetic polymers, aliphatic polyesters are very attractive because they may combine biocompatibility and biodegradability with physical and chemical properties similar to those of commodity polymers[1,2]. In particular, polyesters based on 1,3-propanediol glycol and aliphatic dicarboxylic acids can be prepared with different chain length and high molecular weight[2]. Besides environmental protection and recycling, biodegradable polymers can be used in wound closures, orthopedic implants, drug delivery systems and matrices for cell culture among many other applications. The preparation of ultrathin polymer films (thickness < 100 nm) is essential for some of these developments. In general, polymer ultrathin films can exhibit different structure and properties than either thick films or bulk materials. Polymer thin films are important for applications such as adhesion, surface wetting and liquid crystal alignment. The knowledge of the mechanism and the underlying forces involved in dewetting is crucial to predict stability conditions for practical use[3]. In addition, thin polymer films introduce two dimensional spatial confinement which may affect the molecular order[4] crystallization behaviour[5,6], the morphology[7] or even the crystalline structure[8]. In this presentation we will report on recent research on the structure and morphology of a series of ultrathin and thin films of linear aliphatic polyesters[2] including poly(propylene succinate), poly(propylene glutarate) and poly(propylene adipate) prepared by spin-coating over Silicon substrates. We have combined experiments in the real space by means of Atomic Force Microscopy (AFM) and in the reciprocal space by means of X-ray scattering. Grazing incidence scattering at small and wide angles were accomplished at HASYLAB (Hamburg, Germany) and at ESRF (Grenoble, France) respectively by using X-ray synchrotron radiation. GISAXS and AFM measurements for films thinner than 70 nm show dewetting patterns (Fig.1).

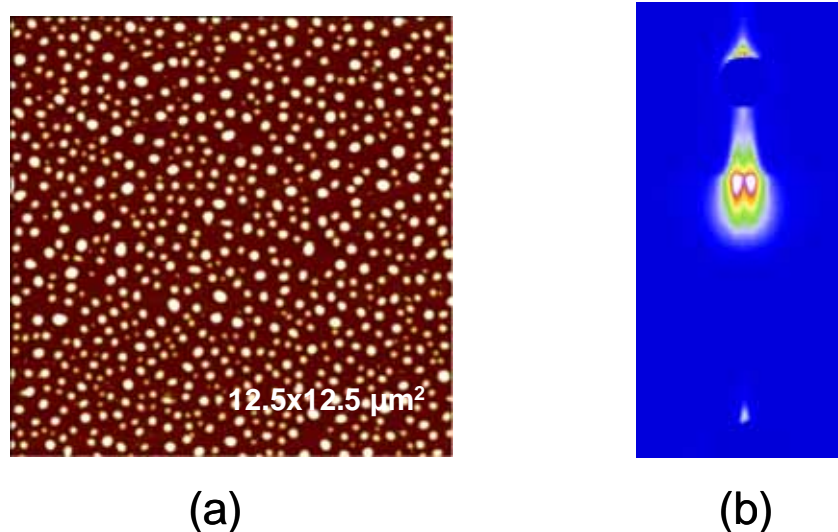


Fig.1. Sample of Poly(propylene adipate) prepared by spin-coating over Silicon substrate. Thickness ≈ 10 nm. (a) AFM image and (b) GISAXS with incidence angle of 0.4° .

Thicker samples exhibit spherulitic morphology with significant amount of edge-on lamellar crystals as revealed by AFM (fig.2a), GIWAXS (fig. 2b) and SAXS experiments in GISAXS geometry using incidence angle $\alpha_i = 0^\circ$ (fig. 2c).

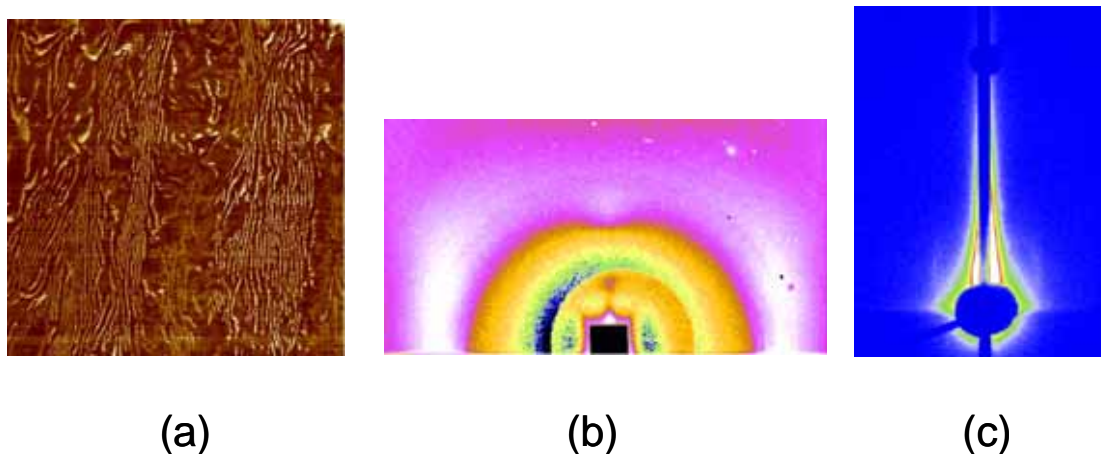


Fig.2. Sample of Poly(propylene adipate) prepared by spin-coating over Silicon substrate. Thickness ≈ 120 nm. (a) AFM image, (b) GIWAXS with incidence angle of 0.36° . (c) SAXS in GISAXS geometry with incidence angle of 0° .

SAXS experiments in GISAXS geometry with $\alpha_i = 0^\circ$ were also performed during in situ crystallization. A fast structural organization with a predominant edge-on lamellar crystal orientation was observed during crystallization at high undercooling conditions. This can be understood assuming that edge-on lamellae develop at the film surface because homogeneous nucleation at the surface is faster than close to the substrate[7]. Lamellar crystal edge-on morphology seems to be a rather robust characteristic of the investigated aliphatic polyester thin films.

References

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