Nanostructure of crystallizing polymer thin films

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INTRODUCTION

Polymer chains in thin films show significantly different structures and properties than thick films and bulk materials. Polymer thin films are important to many applications such as adhesion, surface wetting and dewetting, and liquid crystal alignment. On one hand, the knowledge of the mechanism and the underlying forces evolved in a dewetting pattern would enable us to predict stability conditions for practical use. On the other hand, thin films introduce one-dimensional spatial confinement of polymers which affects their crystallization behavior. It is well known that polymer crystallization is initiated by crystal nucleation, and such spatial confinement will significantly lower the formation of crystal nuclei. On the other hand, flat walls may induce a preferentially parallel orientation of the conformations of the polymers in contact with these walls.
This contribution will cover recent research on both topics: dewetting and crystallization in thin films of linear aliphatic polyesters prepared by spin coating on Si-substrates.

EXPERIMENTAL

Sample preparation

Poly(propylene succinate) PPA — T_g = -52°C, T_m = 40°C

Poly(propylene glutarate) PPG — T_g = -47°C, T_m = 54°C

Poly(propylene succinate) PPS — T_g = -27°C, T_m = 44°C

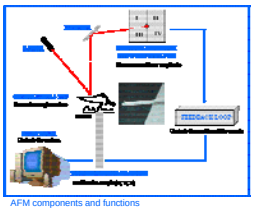
Thin polymer films were obtained from solutions in Chloroform (40 gl^{-1}), used to prepare more diluted solutions with concentrations of 20, 13.3, 8, 4.4, 2.3, 1.2 and 0.6 gl^{-1}

Films with different thicknesses were obtained by spin coating: 0.1 ml of each solution is instantly dropped by a syringe on a rectangular Silicon wafer (100) placed in the center of a rotating plate.

Values of thickness measured by ellipsometry and AFM range from 10 to 400 nm.

Sample caracterization

Atomic Force Microscopy (AFM)



AFM components and functions

Samples were studied by using an Atomic Force Microscopy (Nanoscope IIIa from Veeco) operating in "tapping mode"

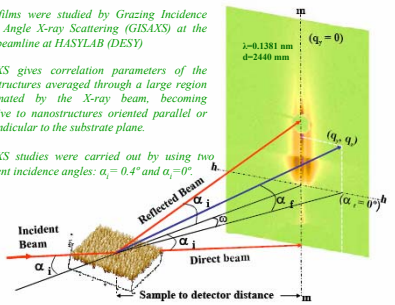
AFM provides high resolution imaging of surfaces in the range of few nanometers to several micrometers.

Grazing Incidence Small Angle X-ray Scattering (GISAXS)

Thin films were studied by Grazing Incidence Small Angle X-ray Scattering (GISAXS) at the BW4 beamline at HASYLAB (DESY)

GISAXS gives correlation parameters of the nanostructures averaged through a large region illuminated by the X-ray beam, becoming sensitive to nanostructures oriented parallel or perpendicular to the substrate plane.

GISAXS studies were carried out by using two different incidence angles: α_i= 0.4° and α_i=0°.

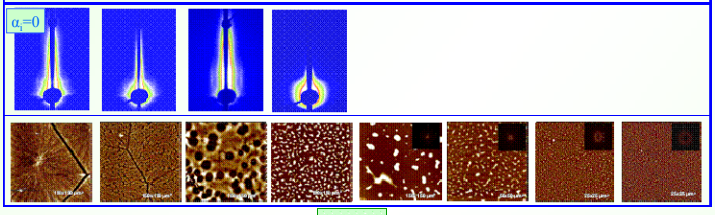


RESULTS

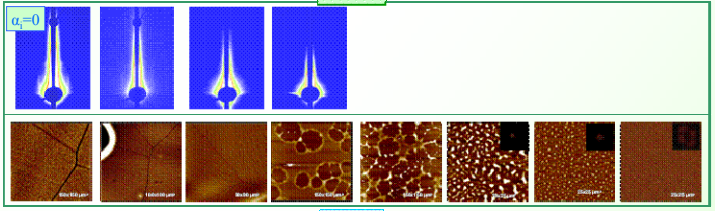
PPA

α_i=0.4

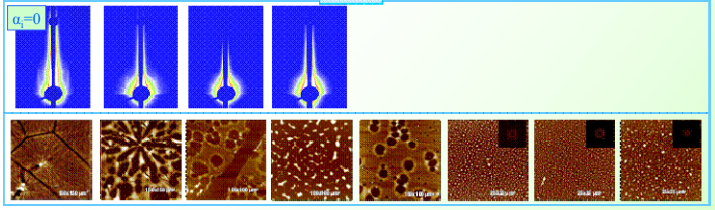
GISAXS experiments with an incidence angle α_i= 0.4° (twice the critical angle for Si substrate) were performed. A maximum in the scattered intensity is only shown in the pattern corresponding to the thinnest PPA sample. This maximum is related to the correlation length between dewetted droplets.
In order to get information about the lamellar nanostructure showed by AFM for the thicker samples, GISAXS experiments with an incidence angle α_i= 0° (transmission geometry) were carried out. Patterns collected in this geometry present a clear maximum in the scattered intensity.



PPG



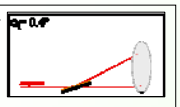
PPS

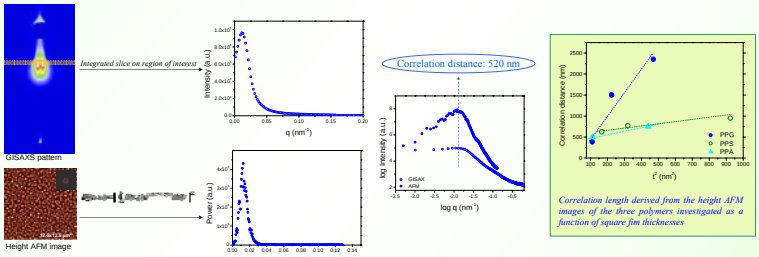


40 gl^{-1} (≈400 nm) 20 gl^{-1} (≈180 nm) 13.3 gl^{-1}(≈85nm) 8 gl^{-1}(≈4.5) 4.4 gl^{-1}(≈2.5nm) 2.3 gl^{-1}(≈1.4nm) 1.2 gl^{-1}(≈1.2nm) 0.6 gl^{-1}(≈0.9nm)

Dewetting:

AFM images show dewetting patterns for samples of the three polymers investigated when the film thickness is smaller than approximately 100 nm.
A maximum in the scattered intensity is only present in the GISAXS pattern taken at α_i=0.4° corresponding to the thinnest PPA sample. In this case the correlation distance between droplets is appropriate to be measured in the q range of the set-up used in the experiment.
GIUSAXS measurements would be of interest in order to complete this study.
AFM results give valuable information on the dewetting morphology and the appropriated analysis of the images gives quantitative results in good agreement with GISAXS data.



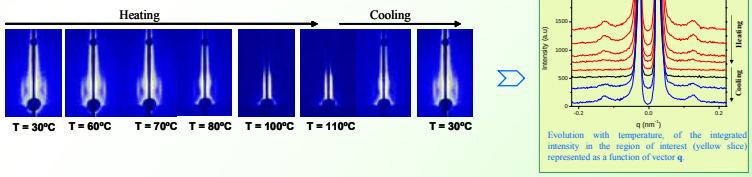


Correlation length derived from the height AFM images of the three polymers investigated as a function of square fim thicknesses

Crystalline nanostructure:

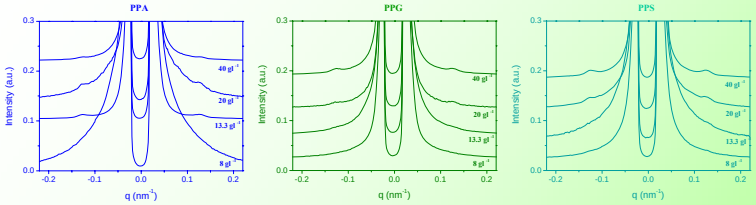
As it has been pointed out previously, the patterns taken at α_i= 0° ("non conventional" GISAXS geometry), show a clear maximum in the scattered intensity. In order to elucidate the nature of such a maximum, we performed melting and recrystallization "in-situ" experiments. Here we present as an example the evolution of the scattering patterns for the PPA (20gl-1) sample. From these experiments it seems that the maximum in the scattered intensity is related to the crystalline lamellae long spacing which disappears upon melting.

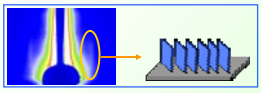
Next experiment shows the evolution of the scattering patterns when a sample of PPA (20gl^{-1}) is heated well above its melting temperature and then is brought back to room temperature.
The behavior of the maximum in scattered intensity seems to be related with the evolution of crystalline structures in the sample.



Evolution with temperature of the integrated intensity in the region of interest (yellow slice) represented as a function of vector **q**.

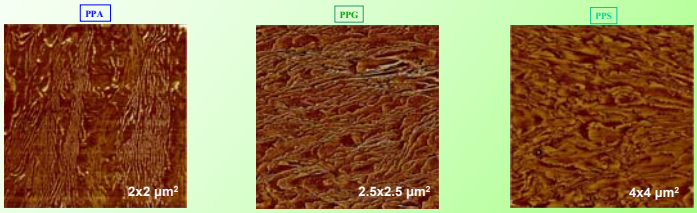
Bellow are presented the intensity profiles, obtained by integrating the region of interest of 2D-patterns, as a function of thickness for the experiments performed at α_i= 0° and RT



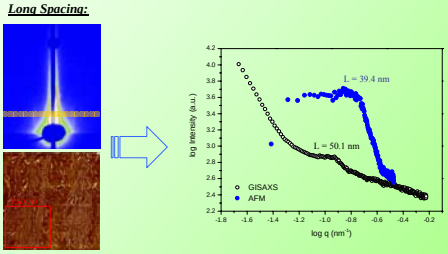


The shape of the maximum in the scattered intensity show a clear lateral structure correlation at q_y = 0.123 nm-1 (L = 51 nm). This fact supports a preferential orientation of the crystalline lamellae perpendicular to the substrate ("edge on" configuration). Nevertheless, AFM images (see bellow) show the "edge on" configuration for the PPA sample but mainly the so called "flat on" configuration (lamellae lying parallel to the substrate) for PPS and PPG samples. This disagreement between GISAXS and AFM results could be explained considering that GISAXS gives information on the nanostructure along the complete thickness of the samples, while AFM gives information on the outer surface only. So the "edge on" configuration could be present in the inner part (in contact to the substrate) of all PPA, PPS and PPG films but in the case of PPS and PPG the interaction of polymer chains with the substrate is lost at the near surface of films and hence the "edge on" configuration is transformed in a "flat on" configuration of crystalline lamellae.

AFM phase images showing characteristic crystal morphology for samples of the three polymers with a concentration of 20gl^{-1}.



Long Spacing:



The "edge on" configuration of PPA crystalline lamellae (as seen by AFM) allows measuring the characteristic Long Spacing and correlating this value with the one obtained by GISAXS (α_i= 0°).

ACKNOWLEDGEMENTS

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