ESRF	**Experiment title:** Near-Surface Crystallization in Highly Oriented and Nanostructured Polymer Films	**Experiment number**: SC-1998
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Report:

The aim of the experiment is to investigate the structure and the orientation of a Polycarbonate thin film at various stages of its crystallization from the polymeric surface pre-oriented by rubbing. Also of interest is to analyse the evolution of the surface roughness during the growth of the crystalline phase. Grazing incidence measurements of the specular reflectivity and of the wide angle diffraction were performed on beamline ID10B at wavelength 1.4886 Å, on 5 different samples elaborated *ex situ.* The samples were prepared as follows : spincoating of the polymer solution on a silicon wafer, unidirectional velvet rubbing at room temperature for 1 min and subsequent exposure to solvent vapor for 0, 2, 3, 4 or 6 min. The specular reflectivity pofiles of Fig. 1 clearly show that the roughness of the film surface first decreases before increasing as the crystallization proceeds. A detailed analysis of the reflectivity data is in progress.

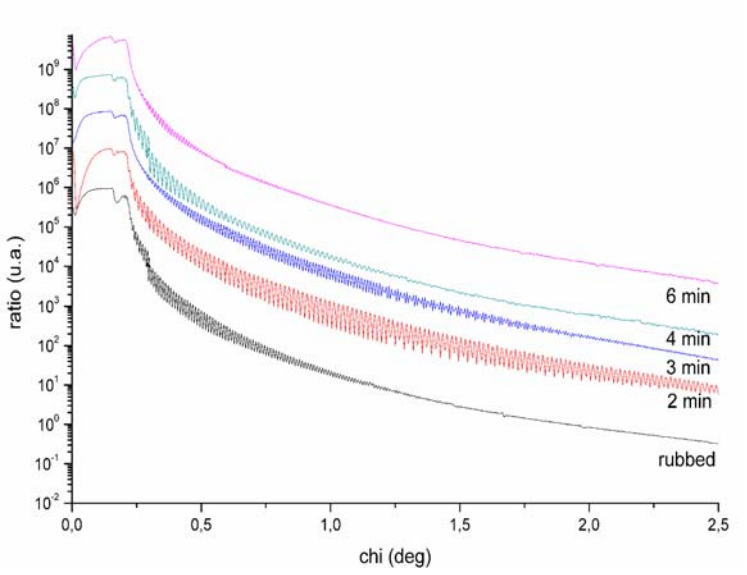

Figure 1
Evolution of the reflectivity of rubbed polymer films (300nm) on a Si(100) substrate upon solvent induced crystallization. The exposure times correspond to different durations of the crystallization process. Damping of the Kiessig fringes is related to the roughness of the interfaces. The short exposure time shows a smoothening of the film attributed to a plasticizing effect of the solvent. For solvent exposure times ≥3min one observes an increase of the roughness due to the crystallization process in the bulk of the polymer film.

Wide angle diffraction from the crystalline phase and diffuse scattering from the amorphous phase were recorded for different grazing incidence angles χ in order to probe either the surface ($\chi<\chi_c$) or the bulk of the polymer film ($\chi>\chi_c$). As the critical angle of total reflectionon the polymer is $\chi_c = 0.15$ deg., one can evalute the penetration depth of the X-ray beam to be of the order of 6nm for $\chi = 0.10$ deg and 60 nm for $\chi = 0.15$ deg., while it is much larger than the film thickness for $\chi = 0.18$ deg.

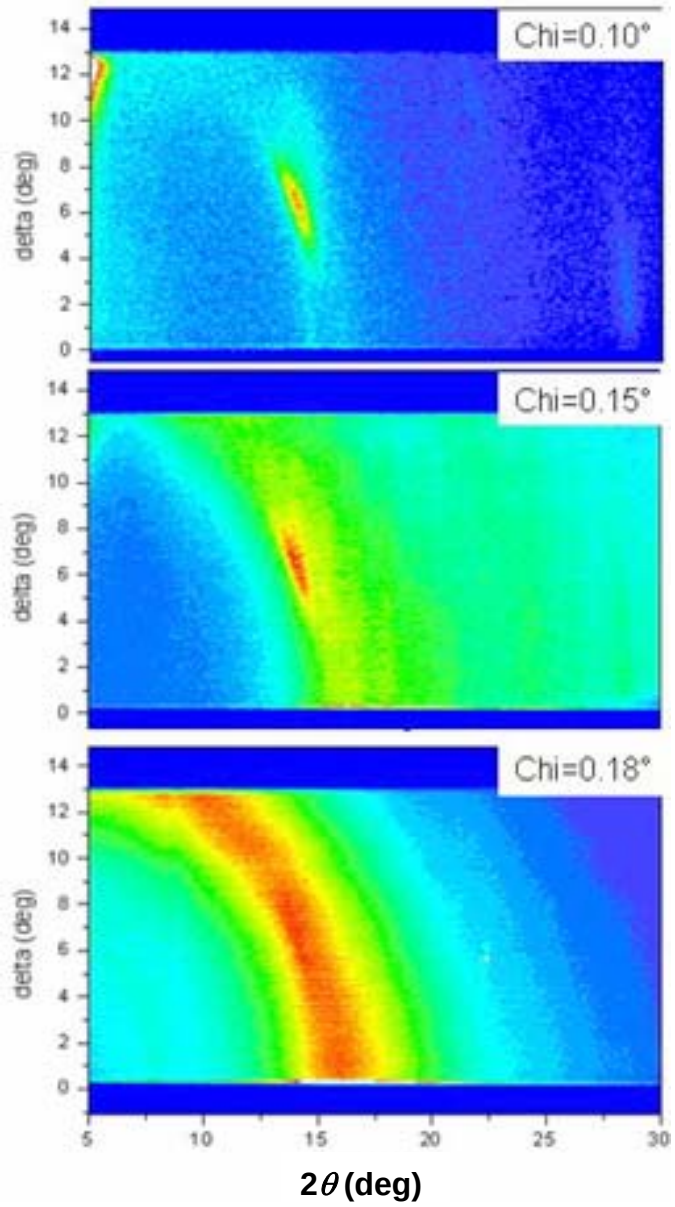

Figure 2
Grazing incidence X-ray diffraction patterns performed at various incidence angles χ on a thin polymer film consisting of an oriented crystallized top layer on bulk amorphous underlayer (film exposed 6 min. to solvent vapor). The scans were obtained using a vertical PSD perpendicular to the horizontal film in a (θ, 2θ) geometry, the orientation $\theta = 0$ corresponding to the incident beam parallel to the rubbing direction. The scans obtained for $\chi \leq \chi_c = 0.15$ deg. reveal the typical (210) reflection of the crystallized polymer top layer, whereas for $\chi = 0.18$ deg. only the amorphous halo from the underlayer is observed

During this first series of experiments we have searched for (hk0) Bragg reflections keeping the rubbing direction, which is expected to be the chain axis (001) in the bissector plane (θ, 2θ scans) . The results displayed in Fig. 2 show a textured Bragg reflexion from the surface layer ($\chi = 0.10$ deg and 0.15 deg.) which almost disappears in the bulk ($\chi = 0.18$ deg.). The Bragg angle $2\theta_B = 15.5$ deg corresponds to the (210) reflection of the monoclinic phase of polycarbonate[1].
Moreover, the small orientation distribution around the exit angle $\delta = 6.5$ deg indicates that the (210) planes are tilted by ≈ 25 deg. with respect to the normal, suggesting that there is a preferential orientation of the (010) dense planes of PC parallel to the plane of the Si(100) substrate. This result is unexpected and new since usually, rubbing or drawing of a polymer film induces a fiber symmetry and not a biaxial orientation.
Rocking curves of the sample (ω scans around the normal at the Bragg peak position) give also an order of magnitude of the angular distribution of the chain axes on each side of the rubbing direction :
$\Delta\omega \approx 25$ deg (full width at half maximum).
Similar results, but with lower intensity of the (210) Bragg reflection have been obtained for the samples with shorter exposure time to solvent vapor (4 min., 3 min. and 2 min.) and a quantitative analysis of the data is in progress. Moreover a reliable texture analysis needs more than a single Bragg reflection and a second series of experiment would be required.

At present, we have obtained a first analysis of the surface roughness evolution, an evaluation of the thickness of the semi-crystalline layer ≈ 50 nm, and an idication on the preferential orientations of the crystal axes **a** and **c** in the plane of the film, with **c** roughly along the rubbing direction.

Reference

(1) R. Bonart, *Die Makromoleculare Chemie*, **92,** 149 (1966)