Layered structure in main chain dibenzo-18-crown-6 ether polymers by simultaneous WAXS/MAXS-SAXS/DSC and by GISAXS measurements

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The structure and thermal properties of polymers containing dibenzo-18-crown-6 ether units in the main chain linked to an aliphatic spacer of different length (C10 or C14) is reported. X-ray diffraction patterns of all the studied samples exhibit a peak in the medium angle region, revealing the existence of a lamellar structure. Simultaneous calorimetry and small, medium (SAXS-MAXS) and wide (WAXS) x-ray measurements during cooling and subsequent heating of the samples reveal that a layer phase is formed upon cooling. In the case of the homopolymers, this phase is almost simultaneously accompanied by the appearance of some reflections in the wide angle region as an indication of lateral crystallization. However, by copolymerization, the formation of the layer phase is decoupled from lateral crystallization, being stable in a wide temperature region.
The perfection of this layered structure is more evident in thin films when the main chain dibenzo-18-crown-6 ether polymers are prepared in the form of thin films (9-70 nm) prepared from chloroform solutions by spin coating on a silicon substrate. The quality of the polymer coatings was revealed by their reflectivity spectra. The grazing incidence medium angle X ray scattering (GIMAXS) results revealed that polymer chains lie completely parallel to the silicon substrate surface because of the presence of the medium angle reflection, related to the polymer repeating unit but there is no signal for any lateral organization of higher scale size. Grazing incidence small angle X ray scattering (GISAXS) results, particularly for the thicker coating samples, revealed structure correlations in plane with length scale sizes around 13 nm provoked by resonant diffuse scattering effect.

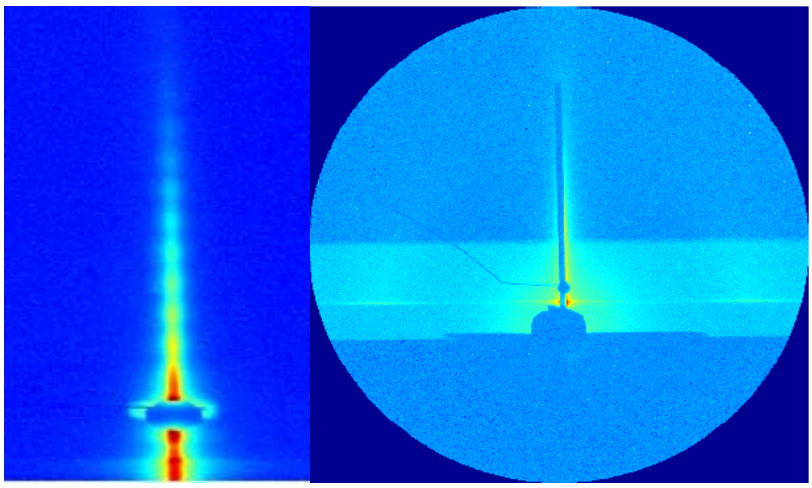

Figure 1: (Left) Reflectivity bands observed by grazing incidence at small angle. (Right) Grazing indicence at medium angle. A clear sharp reflection is observed indicating the existence of molecular order parallel to the film surface