Report on experiment SC-3171 performed at ESRF on ID10B – June 2011

Title : X-ray reflectivity study of the influence of SuperCritical scCO2 on CO2 philic and CO2 phobic thin films at surface

The aim of this experiment was to measure X-ray reflectivity of different materials submitted to CO2 under pressure either in the liquid or supercritical state. 2 sets of experiments have been carried out.

1- Condensation of CO2 on silicon

The experiment first started with some problems related with a bad pressure sensor which was not calibrated on the high pressure cell which yields a loss of one day of experiment.
We first measured the influence of condensation of CO2 on a glass substrate at 15°C with a critical pressure of 50.8 bars. We found out that on the first elevation of pressure the glass substrate was initially covered by a water layer. On pressure uptake this layer progressively adsorbed CO2 and was clearly swelling. When passing the gas liquid transition this water layer was removed and the second run of CO2 pressure was clearly evidencing that almost no CO2 layer was condensing on the substrate (on the contrary to what was published by other groups). In addition we evidenced that the pressure at which CO2 transforms from the gaseous state to liquid state is not constant. Indeed mestastable state develops inside the cell. When moving quickly we observe a transition at 49.6 bars while at slow changing pressure rate we observe a change at 48.5bars. **Moreover, we observed an hysteresis between the gaseous-liquid and the liquid-gaseous transition pressures. This shift was function of the pressure slope and highlights again the metastable state of CO2.** This experiment was stopped for this reason.

2- Swelling of PS thin films as a function of CO2 pressure.

The next experiment consisted in measuring the swelling of polystyrene (PS) ultrathin films exposed to supercritical CO2. Experiments were performed at a constant temperature of 32°C. We slowly increased pressure in the cell so as to cross the border line between gas and supercritical state.
As shown in Figure1, we observed the progressive swelling of the polymer due to CO_2 uptake inside the film. The swelling is accompanied by a decrease of the electron density of the film since the electron density of PS (344e/nm^3) differs from the one of sc CO_2 (196e/nm^3). The swelling can be followed pretty well up to 70 bars.

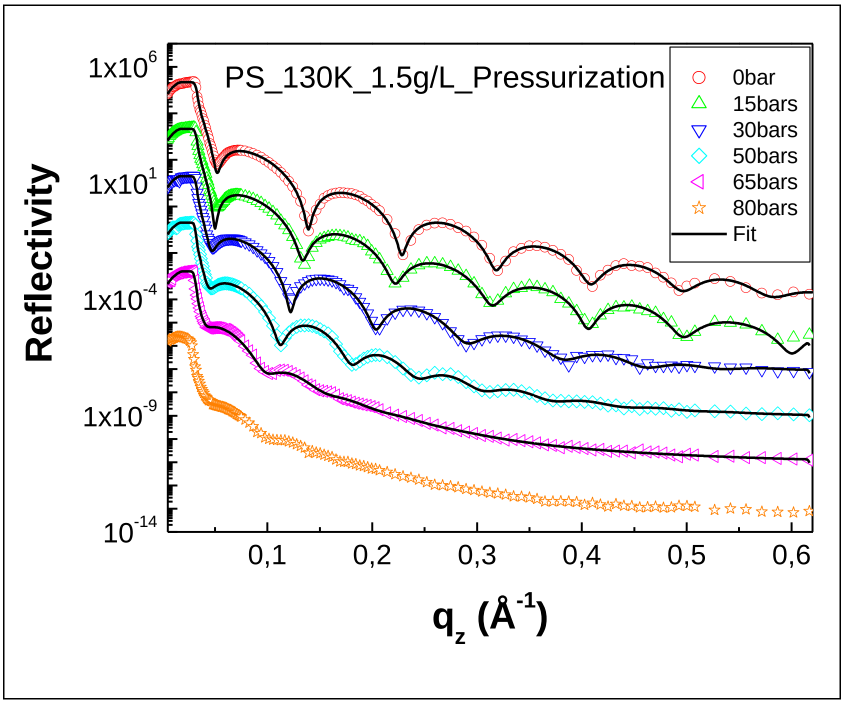

Figure 1 : Evolution of the PS film as a function of CO2 pressure inside the cell during CO2 uptake. The period of Kiessig fringes progressively decreases and their amplitude almost vanishes.

Above 73.5 bars, CO_2 is in a supercritical state and its mass density increases significantly from 241kg/m^3 at 70 bars to 652kg/m^3 at 80 bars. This drastic change of density also produces a correlative change of electron density of CO_2 which passes from 73e/nm^3 to 196e/nm^3 (qc=0.0167Å^{-1}) as shown in Figure 2 .

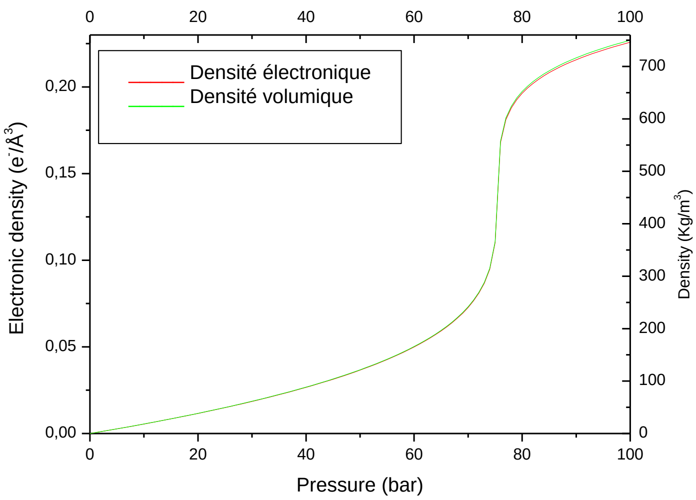

Figure2 : Change of electron density of CO_2 and mass density of CO_2 as a function of pressure showing the rapid evolution of these two parameters around the supercritical point at 73.5 bars.

The contrast between the electron densities of CO_2 and PS is therefore changing significantly when one passes from the gas to the supercritical state. As it can be seen in

Figure 2 this diminution of contrast yields an almost complete disappearance of the Kiessig fringes of the film. This disappearance is in agreement with the reduction of the derivative of the electron density at the film/CO_2 interface which has a twofold origin : i) the uptake of CO2 inside the film which reduces accordingly the total electron density of the film and ii) the increase of the electron density of CO2 with pressure.

In addition we have monitored the evolution of the film thickness during CO2 sorption and desorption. A typical example is shown in Figure 3. In this example one can clearly observe that the film does not recover its initial state but remains swollen after returning to atmospheric pressure. A constant feature seen in our measurements (disagreeing with previous studies) is the fact that the strongest change in thickness of the film is seen from 50 bars up. This shows that the gaseous state allows a significant swelling of the film and that the supercritical state is not compulsory to observe this effect.

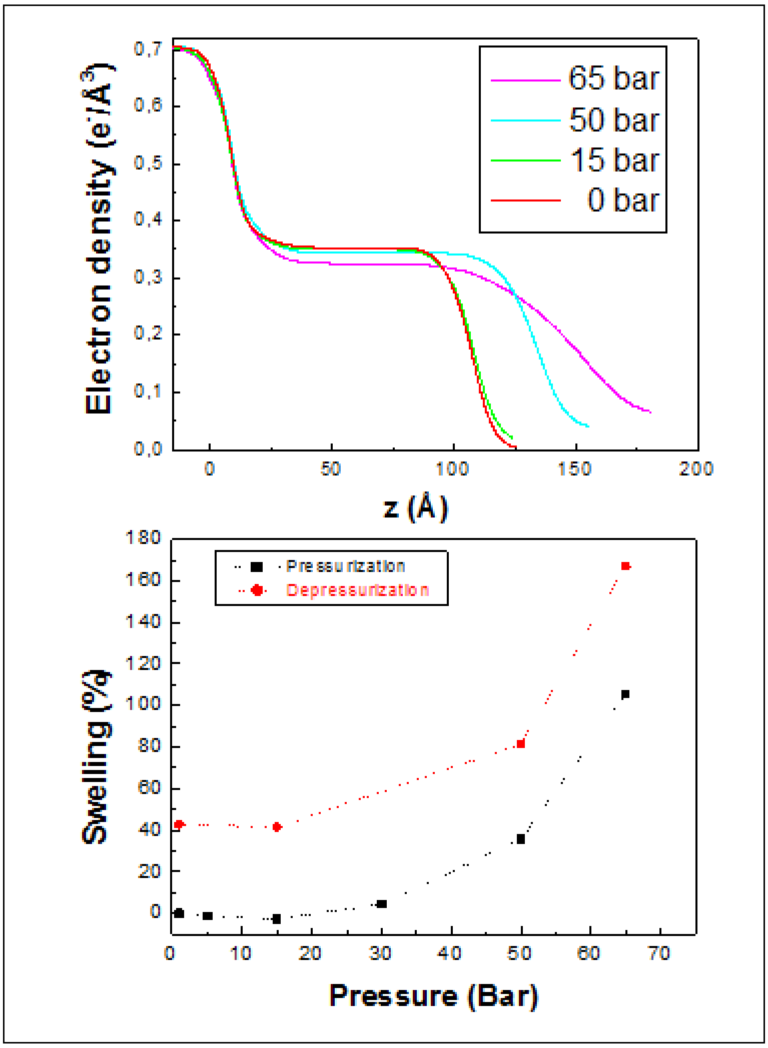

Figure 3: Evolution of electron density of the film during depressurisation (top panel) together with the evolution of the swelling as a function of pressure (bottom panel)

Experiments performed on 2 films with different thickness have shown that the onset of swelling for a thin polymer film depends on its thickness. For the film shown in Figure 2 one can see that the pressure at which occurs the swelling is close 40 bars. We believe that this pressure is related to the pressure at which the glass transition occurs in the confined film. The thinner the film and the lower this pressure.

All these observations are going to be submitted as a full paper in Macromolecules soon.