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X-Ray Scattering Study of Nano-Polymer under Supercritical CO_2

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Despite the negative image of carbon dioxide (CO_2) due to his controversial contribution to global warming, this chemical compound in its supercritical state (sc-CO_2) is used as a green non-toxic solvent of low cost. The supercritical state of CO_2 occurs as soon as temperature and pressure (T, P) are raised above the critical values (T_C = 31°C, P_C = 73.8 bar). In the supercritical state, CO_2 exhibits particular characteristics such as a liquid-like density and highly penetrable gas-like diffusivity. Such properties favor the absorption and diffusion of CO_2 inside polymer thin films causing swelling of the polymer and thereby affecting certain properties such as density, roughness and glass transition temperature. We report here in-situ X-Ray Reflectivity (XRR) and GISAXS studies of polymer as thin films and nano-island isothermally exposed to CO_2 as a function of CO_2 pressure starting from ambient pressure up to the supercritical state. Swelling of Polystyrene confined films is investigated by this technique. Our experiments show that these films swell when exposed to CO_2 . An increase of the interfacial roughness is also observed when CO_2 pressure is raised. We assume that it is due to random movements and disentanglement of the chains at the top surface. This increase in roughness combined to a decrease of the contrast of electron density between the film and pressurized CO_2 makes it difficult to measure XRR curves at high pressure for ultrathin film. However this effect is less noticeable in thicker films.
The results for thin films reveal a universal dependence of swelling with the CO_2 density only at low pressures. At high pressure the swellability depends on the density fluctuations of CO_2 . We also evidence a hyper-swelling (260%) for nano-island, even further enhanced in the supercritical state.