Photochromism of spirooxazines in mesoporous organosilica films

Lorraine Raboin, Muriel Matheron, John Biteau, Thierry Gacoin, Jean-Pierre Boilot

Supplementary Data

Structural characterization

As previously observed in similar experimental conditions, CTAB-templated films present the 3D-hexagonal structure belonging to the $P6_3/mmc$ space group (Figure 1S) while Pluronic 6800 (Figure 2S) and Pluronic 10400 (Figure 3S) copolymer-templated films respectively exhibit orthorhombic structure belonging to the Fmmm space group and distorted 2D-hexagonal structure with the c2m centred rectangular space group. All these structures have been described in details in previous papers [ref. 13-15 and 19-20 of the paper].

Figure 4S shows the GISAXS pattern corresponding to organosilica HMDS-grafted 40% $MeSiO_{1.5}$ films which present a well organized structure corresponding to the 3D-hexagonal structure with the $P6_3/mmc$ space group.

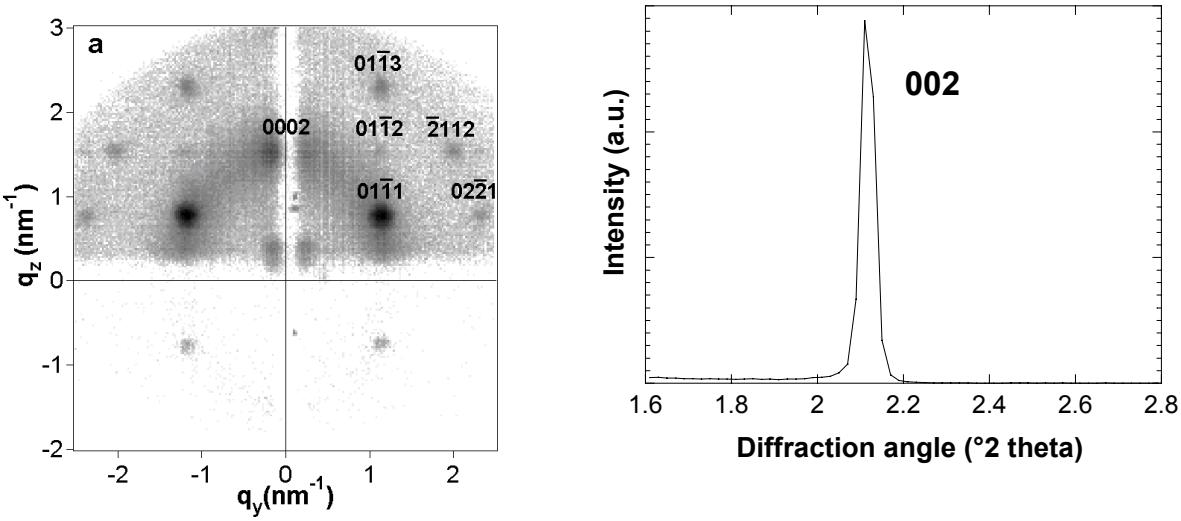


Figure 1S. GISAXS (left) and XRD patterns (right) for 3D-hexagonal mesostructured films prepared with the CTAB as template. The indexes of the reflections belong to the $P6_3/mmc$ space group.

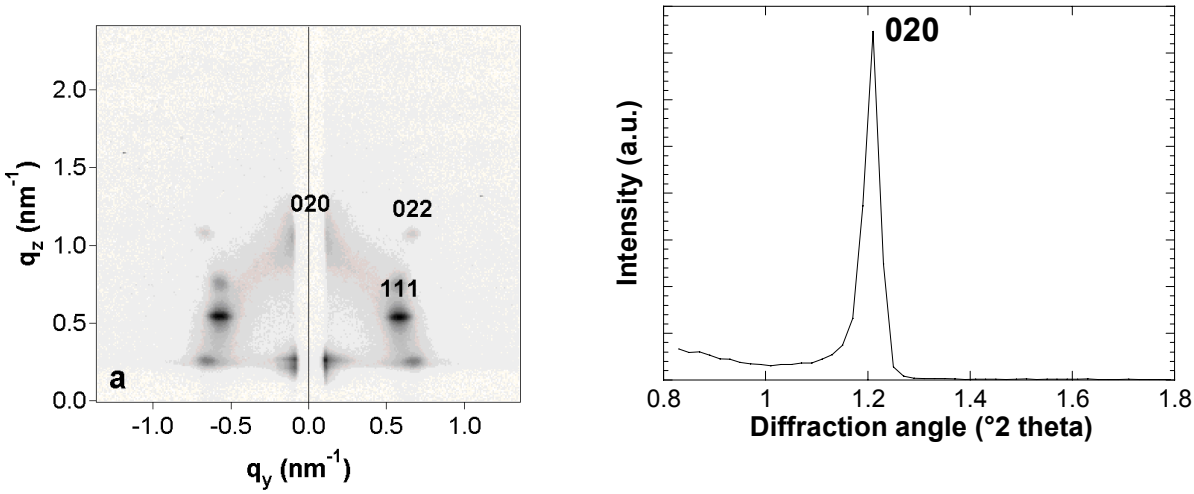


Figure 2S. GISAXS (left) and XRD patterns (right) for orthorhombic mesostructured films prepared with the PE6800 copolymer as template. The indexes of the reflections belong to the Fmmm space group.

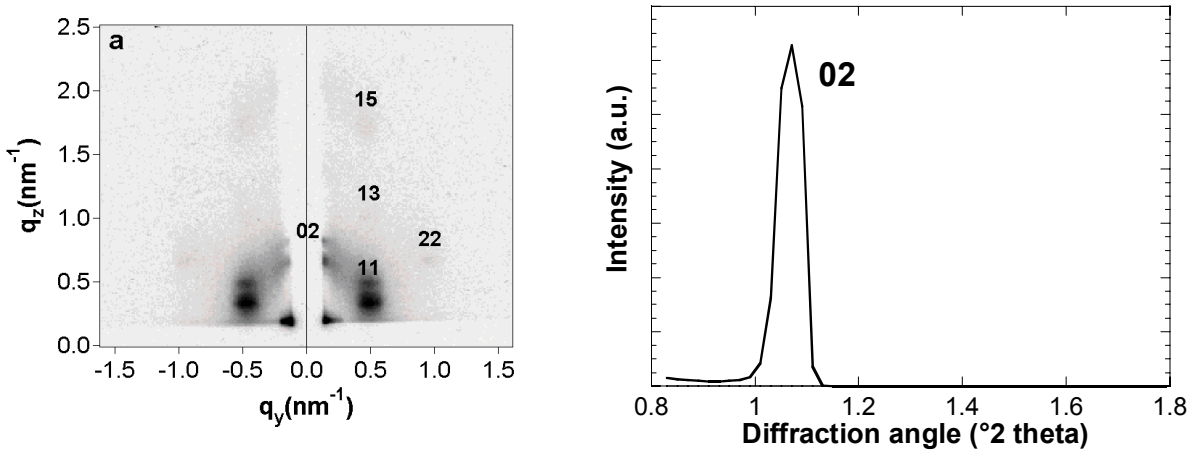


Figure 3S. GISAXS (left) and XRD patterns (right) for 2D-hexagonal mesostructured films prepared with the PE10400 copolymer as template. The indexes of the reflections belong to the c2m centred rectangular space group.

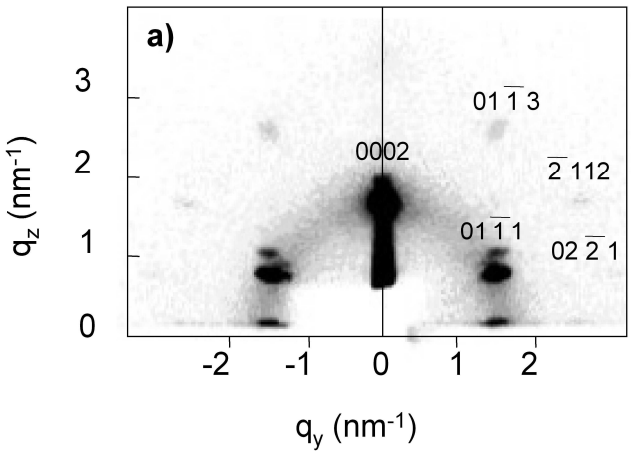


Figure 4S. GISAXS pattern for 3D-hexagonal organosilica mesoporous films (HMDS-grafted 40% $MeSiO_{1.5}$ films). The indexes of the reflections belong to the $P6_3/mmc$ space group.

Porosity characterization in 3D-hexagonal mesoporous films

In order to probe the porosity of the films, the samples were introduced in a vacuum cell, which was fitted on a visible ellipsometer for in situ measurements. The vapor pressure (ethanol) was progressively increased until saturation to measure the adsorption branch and decreased to obtain the desorption one. Figure 5S displays the isotherms obtained for 3D-hexagonal mesoporous films. The capillary condensation occurring at low pressure is characteristic of the micropore filling, and the height of this condensation step is proportional to the amount of micropores. While the silica films contain a large amount of micropores, the microporosity decreases in organic-inorganic hybrid films. HMDS-grafted films present high refractive index values before the introduction of ethanol as about 75% of micropores disappear during the post-grafting reaction. In contrast, "organosilica HMDS-grafted 40% $MeSiO_{1.5}$ films" show a very low initial index and are as porous as pure silica ones.

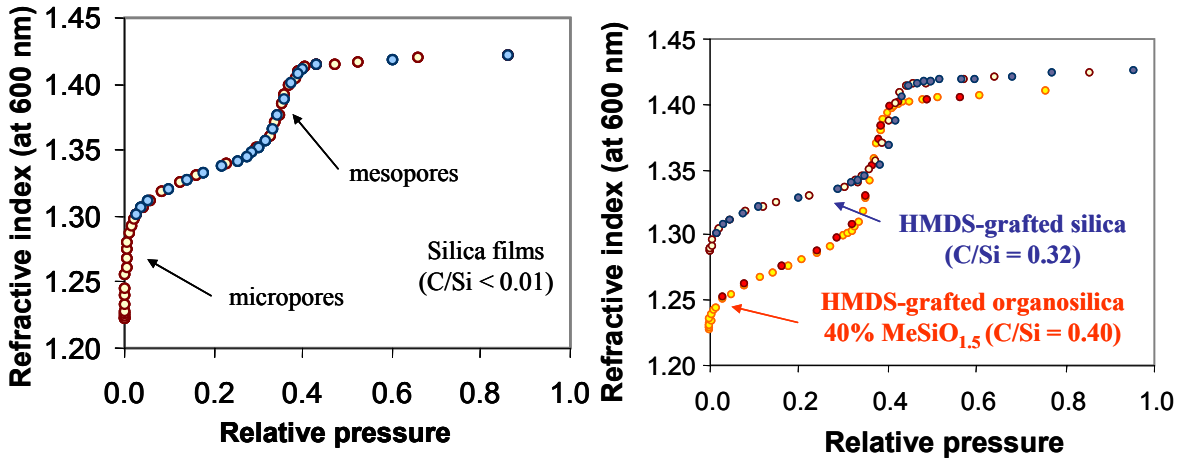


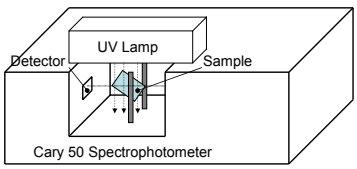
Figure 5S. Ethanol adsorption-desorption isotherms at 25°C on different 3D-hexagonal films. The C/Si molar ratio in films was deduced from Rutherford backscattering / nuclear reaction analysis.

Irradiation conditions and spectroscopic measurements

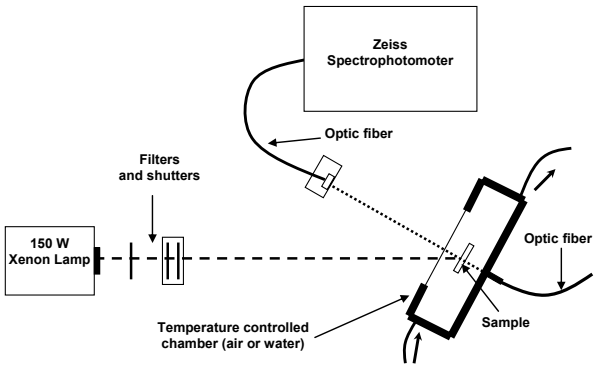
Samples were optically characterized by two methods.

(1) The experimental setup for standard optical characterizations at room temperature is shown in Figure 6Sa.

(2) A schematic experimental setup for kinetics measurements at various temperatures is depicted in Figure 6Sb. Figure 7S shows Arrhenius plots for different SO-doped films.



a)



b)

Figure 6S. Schematic representation of the two apparatus used for the kinetics measurements performed on photochromic films.

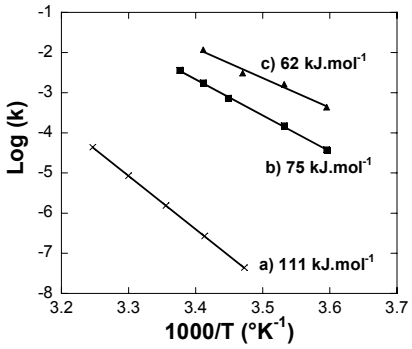


Figure 7S. Arrhenius plots and deduced activation energies of the thermal bleaching for a) SO1 in soft organosilica films (50 MeHSiO –50 $MeSiO_{1.5}$ (t_g = - 45°C)), b) SO2 in 3D-hexagonal mesoporous films (HMDS-grafted 40% $MeSiO_{1.5}$, c) SO2 in 2D-hexagonal mesostructured film (Pluronic 10400 template).