

## Photo-Orientation of Mesoporous Silica Materials via Transfer from Azobenzene-Containing Polymer

### Monolayer

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### 1) Detailed Descriptions of Experimental Procedures

**Materials.** The chemical structures of the materials used in this work are shown in Figure 1. The synthetic procedure for an Az-containing amphiphilic polymer (6Az10-PVA) was described in the previous reports.<sup>31,32</sup> Poly(di-*n*-hexylsilane) (PDHS) was prepared by reductive condensation of the dihexyldichlorosilane with sodium metal in dry toluene.<sup>33</sup> Molecular weight was determined by gel permeation chromatography analysis (JASCO Intelligent UV/vis detector 875-UV with Integrator 807-IT) using polystyrene as the calibration standard. PDHS samples of different molecular weights were prepared by solvent fractionation from toluene, using 2-propanol or methanol as the poor solvent. A dichroic diaminoanthraquinone dye (LCD118) was donated by Nippon Kayaku Co., Ltd. 4'-pentyl-4-cyanobiphenyl (5CB) was obtained from Dainippon Ink and Chemicals, Inc. Fused silica plates were cleaned with saturated potassium hydroxide/ethanol and then ethanol followed by washing with pure water (Milli-Q).

**6Az10-PVA Monolayer.** The monolayer of an Az-containing amphiphilic polymer (6Az10-PVA) was transferred onto a substrate by the LB method.<sup>9</sup> A 6Az10-PVA monolayer was formed on a trough (LAUDA, FW-II) filled with pure water (Milli-Q) at 20 °C by spreading a chloroform solution containing 6Az10-PVA ( $1.0 \times 10^{-3}$  Az unit mol dm<sup>-3</sup>) which was pre-irradiated with UV light (365 nm) for 5 min to allow the cis-Az rich photostationary state. After evaporation of the solvent, the monolayer was compressed at a speed of 1.0 cm min<sup>-1</sup>. The monolayer of cis-isomerized 6Az10-PVA was transferred onto a quartz substrate at a constant pressure which provides a target molecular area (0.4 nm<sup>2</sup> per Az unit), by the standard vertical dipping method.<sup>34</sup> The transfer ratio was virtually unity. The deposition in the cis form is a requirement from the preparation of a highly homogeneous 6Az10-PVA LB monolayer on the substrate. The deposited monolayer was stored in the dark to allow thermal isomerization to the trans form of Az.<sup>35</sup>

The 6Az10-PVA monolayer was then irradiated with non-polarized 365 nm light ( $0.4 \text{ J cm}^{-2}$ ) to enrich the cis-Az content and successively with linearly polarized 436 nm light ( $4.0 \text{ J cm}^{-2}$ ).<sup>9</sup> The light irradiation was performed with a 150 W Hg-Xe lamp (San-ei UV supercure-203S) combined with optical filters for wavelength selection (Toshiba optical filters UV-35/UV-D36A for 365 nm illumination and Y-43/V-44 for 436 nm illumination). Light intensity was measured with an optical power meter (Advantest, TQ8210). This irradiation procedure led to a high degree of orientation of the Az monolayer in the in-plane direction.

**PDHS Films on the 6Az10-PVA Monolayer.** PDHS films (thickness = 40 – 60 nm) were prepared by spincoating from a hexane solution on the surface of the 6Az10-PVA monolayer at 2000 rpm for 20 s. Unless stated otherwise, PDHS of  $M_w = 4.5 \times 10^4$ ,  $M_w/M_n = 1.7$  was used. It was confirmed spectroscopically that the contact with a hexane solution does not disturb the photoinscribed structure of the Az monolayer. The thickness of the PDHS film was controlled by adjusting the concentration of the hexane solution dissolving PDHS. The spincoated film of PDHS on the 6Az10-PVA monolayer was first cooled at 0 °C for 60 min, subsequently annealed at 100 °C for 10 min, and then cooled again. This thermal treatment improved the orientational order of the PDHS film.

**Mesostructured Surfactant/Silica Hybrids.** The mesostructured surfactant/silica hybrid film was prepared according to a modified method described by Yang and co-workers.<sup>25</sup> Tetraethoxysilane (TEOS) was mixed with an acidic cationic surfactant hexadecyltrimethylammonium chloride (CTACl) solution. The mixture was stirred for 2 min at room temperature and transferred into a polypropylene bottle.<sup>25</sup> The molar ratio was TEOS : CTACl : H<sub>2</sub>O : HCl / 0.10 : 0.11 : 100 : 7.0. The substrate described above was held horizontally in the mixture with the Az and PDHS surface downward. The surface of the substrate was covered with another plate set at a 0.2 mm distance using a Teflon spacer. The bottle was sealed at room temperature for 7 days, which allowed the formation of the mesostructured surfactant/silica hybrids. These deposited silica films were washed with pure water (Milli-Q).

**Incorporation with Mixtures of Liquid Crystal/Dye into Mesochannels.** The template surfactant molecules were removed by photocalcination<sup>36</sup> from the photo-oriented mesostructured surfactant/silica composites. The mixture of 5CB and LCD118 (LCD118; 5 wt %) was dropped on these mesoporous silica films. This mesoporous silica film was left for 1 day, and then the substrate was dried in vacuum at 120 °C.

**Measurements.** UV-visible absorption spectra were taken on a Hewlett Packard 8452A diode array spectrophotometer and a JASCO MAC-1 spectrophotometer that is suited for weakly absorbing samples. Microscopic polarized absorption spectra were measured with a HITACHI U-6500 spectrometer. For obtaining polarized spectra, a polarizer mounted in a rotating holder was placed in front of the samples. Fourier transform infrared (FT-IR) spectra were recorded on a Biorad FTS6000 spectrometer. The system was purged with dried air. A silicon wafer was used as the substrate for transmission measurement in the normal incidence.

Microscope observations of the morphology of the mesostructured surfactant/silica hybrids film were carried out by using an Olympus BX-60 optical microscope. The atomic force microscope (AFM) observation was carried out on a SPA300/SPI3700 (Seiko Instruments) in the noncontact mode (dynamic force mode) at ambient atmosphere.

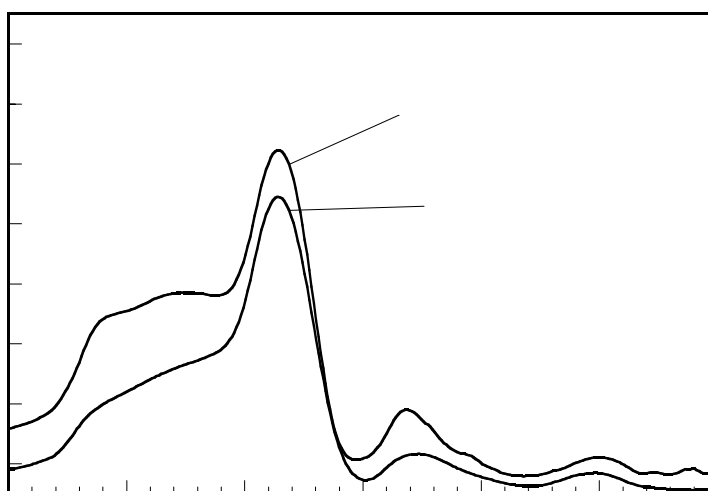
Standard  $\theta$ - $2\theta$  X-ray diffraction (XRD) data were recorded on Philips X'Pert-MPD diffractometer using  $\text{CuK}\alpha$  radiation with a graphite monochromator. A grazing angle in-plane XRD study was performed with an X-ray diffractometer equipped with an open Eulerian cradle goniometer (PW3050). The incident angle of X-rays was set at  $1.0^\circ$ .

Field-emission transmission electron microscopy (FE-TEM) images were recorded on a Hitachi HF-

2000 microscope operating at an accelerating voltage of 200 kV with a typical recording magnification. Samples prepared on a silicon wafer were attached to an epoxy resin. These specimens were mechanically thinned and polished to produce a central region of  $\sim 30 \mu\text{m}$  thick. This region was then milled with two argon ion beams with incident angles of  $-10^\circ$  and  $10^\circ$ , respectively, in vacuum.

## 2) IR spectra around Si-O stretching band.

The spectrum shows some decreases in absorbance after photocalcination, however this change is not essential because the spectral intensity can be originated from the inhomogeneous thickness. We regard that the siloxane network is essentially unchanged before and after the photocalcination process.



**Figure** FT-IR spectra of the mesostructured surfactant/silica hybrids film on the photo-aligned PDHS film. A, As-synthesized; B, After photocalcination.