Photo-Alignment Behavior of Mesoporous Silica Thin Films Synthesized on a Photo-Cross-Linkable Polymer Film

Haruhiko Fukumoto,[†] Shusaku Nagano,[†] Nobuhiro Kawatsuki,[‡] and Takahiro Seki*[,†]

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan, and Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji 671-2201, Japan

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Two-dimensional-hexagonal mesoporous silica thin films with aligned mesochannels in one direction at large scales will be favorably applied in optics, electronics, separation technologies, and so forth. We propose herein a new photo-aligning and micropatterning technique for mesochannels of a silica thin film using a photo-cross-linkable polymer film with a cinnamoyl group. The polymer film was uniaxially photo-oriented by exposure to the linearly polarized UV (LPUV) light. On this film, the mesoporous silica thin film was synthesized by various preparation methods. The orientation of the mesochannels was evaluated by in-plane X-ray diffraction (XRD) measurements. It was shown that the mesochannels were aligned perpendicular to the polarized direction of the irradiated LPUV light. In-plane XRD measurements and transmission electron microscopic and optical microscopic observations of the silica films revealed that photo-orientation of the mesochannels is controlled over the whole surface area of the film. In addition, micropatterning of the photo-aligned mesoporous silica films was readily attained by exposure to the LPUV light passed through a photomask.

Introduction

Organic surfactants show lyotropic liquid crystal nature in aqueous solutions. Several mesoporous silicas such as MCM-41,[1,2] FSM-16,[3,4] and MSM-48[5] have been synthesized as templates of the lyotropic organic surfactant aggregates. These materials possess a large surface area and uniformly sized pores (typically 2−10 nm diameter), for the steric structures of pores as two-dimensional (2D)-hexagonal[1−4] (*P*6*mm*), cubic (*Ia*3*d*,[5] *Pm*3*n*[6]), three-dimensional-hexagonal[6] ($P6_3/mmc$) packing, and so forth. From such structures, mesoporous materials have attracted increasing attention as catalysts[7−9] for larger molecules and also for creation of various functions such as separations, chemical sensing of molecules,[9] and molds of polymers.[9−11]

Thin films of mesoporous silica synthesized on substrates are useful for finding new applications. For example, such films can be applied for optical and electric devices based on incorporation of functional dyes[12] or metal clusters[13] into the nanospaces. In general, nanostructures of the thin films are aligned at local levels but are randomized at larger scales. Development of alignment methods of mesostructures at larger scales is essential to extend applications. One promising alignment method can be an orientational transfer from a surface of an oriented polymer film as widely applied in liquid crystal technology. In fact, synthesis of the *P*6*mm* mesoporous silica film on a rubbed surface[14,15] or Langmuir−Blodgett monolayer[16] of polyimides can be used for orientation of the cylinder channels. Nevertheless, all the above "mechanical" procedures do not benefit from micropatterned orientation.

In this regard, we focused on the photo-alignment technique[17,18] in liquid crystal molecules. Polymer films with functional groups such as the photo-isomerizable azobenzene or the photo-cross-linkable cinnamoyl group can be applied for optical information storage, retardation films, photo-aligment layers for a liquid crystal orientation, and so forth. We have previously attained photocontrols of cylinder meso-

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* To whom correspondence should be addressed. Fax: 052-789-4669. E-mail: tseki@apchem.nagoya-u.ac.jp.

[†] Nagoya University.

[‡] University of Hyogo.

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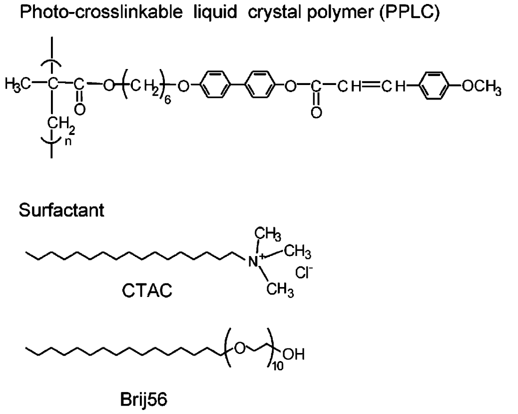

Figure 1. Chemical structure of PPLC and surfactants (CTAC, and Brij56).

channels of a *P*6*mm* mesoporous silica thin film via two-step transfer from a photo-aligned azobenzene polymer monolayer via polysilane film to mesoporous silica film.[19,20] However, the previous process has a weak side from practical viewpoints as follows. (i) The process is complicated and demands handling skills. (ii) The orientation of the composite film does not survive temperatures above 40 °C; therefore, the structure of the channels lacks mechanical stability because of insufficient cross-linking of the siloxane condensation.

To overcome the above problems, we proposed a new versatile photo-alignment method using a photo-cross-linkable side-chain-type polymer with liquid crystal nature (PPLC).[21] We employed poly[6-(4-(4′-methoxycinnamoyloxy)biphenyloxy)hexyl methacrylate] as the PPLC in which the mesogenic biphenyl group is combined with a cinnamoyl terminal (Figure 1). In many types of photo-cross-linkable polymers, an optical anisotropy of angular selective [2 + 2] photodimerization between two cinnamoyl groups proceeds by linearly polarized UV (LPUV) light.[22−24] For PPLC under investigation, the photoinduced orientational anisotropy of the film is largely amplified through the self-assembling nature of the liquid crystal by annealing. For such a property of the PPLC, the film itself can be applied for fabrication of optical memory devices and retardation films.[25,26] Another advantage to use the photo-cross-linkable polymer as the PPLC is that the resultant photochemical cross-linking firmly fixes the anisotropic molecular orientation. This feature is anticipated to allow facile performances of siloxane condensation at higher temperatures without damaging the alignment polymer film. This paper describes the details and features of the photo-alignment behavior of mesochannels of silica film formed on the photo-cross-linkable PPLC film. Factors affecting the structure such as irradiating light energy, choice of surfactant, film thickness of silica, and so forth are varied, and the optimization of this process is discussed.

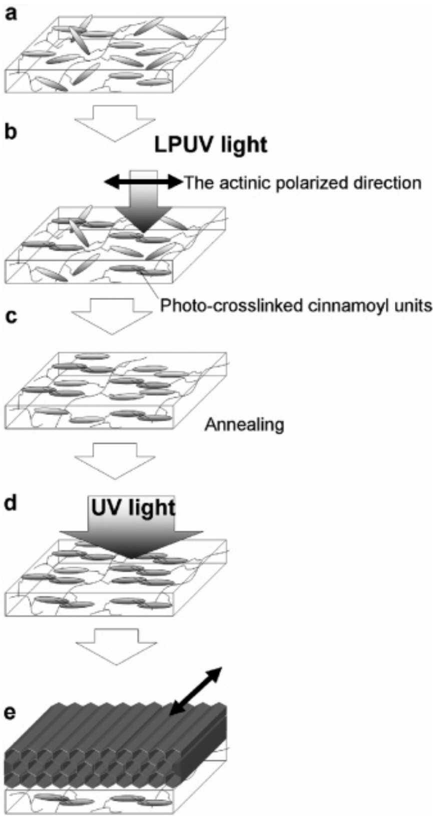

Figure 2. Photo-alignment procedures for the PPLC film and surfactant/silica mesostructured film.

Experimental Section

General Procedures for the Photo-Alignment. The photo-orientation process using the PPLC film is schematically indicated in Figure 2. First, the spin-cast film of PPLC was prepared. The mesogens had random orientations at this stage (Figure 2a). Irradiation of the LPUV light (3.6 J cm^{-2} at 313 nm) to the polymer film induced a slight preferred anisotropy of mesogenic side chains whose optical absorption axis was in parallel to the polarized direction of the LPUV light (Figure 2b). Next, the film was annealed at the liquid crystal phase temperature (150 °C). This procedure brought about high in-plane orientation of the mesogenic side chains in parallel to the polarized direction of the LPUV light (c). Finally, irradiation of the polarized or nonpolarized UV light (1.8 J cm^{-2} at 313 nm using a San-ei Supercure 202S irradiator) to the PPLC film was performed. The unreacted cinnamoyl units underwent the photo-cross-linking, and, thus, the orientation of the mesogenic side chains were strongly fixed (Figure 2d).

The optical anisotropy (degree of molecular orientation) was evaluated by polarized UV absorption spectroscopy using a HP8452A (Hewlett-Packard). For the PPLC film, the order parameter (S, $-1 \le S \le 1$) of in-plane orientation of the side chains is expressed as follows:

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\text{large}} + 2A_{\text{small}}}$$

where A_{large} and A_{small} are the larger and smaller values of $A_{\parallel}$ and $A_{\perp}$.

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Materials. The PPLC film was synthesized according to the method described in the previous paper.[27] The number-average molecular weight (M_n) was about 8.7×10^4 with $M_w/M_n = 2.0$. The polymer adopts the nematic liquid crystal phase above 120 °C and decomposes at 320 °C.

As the templates for the nanostructures, a cationic surfactant, hexadecyltrimethylammonium chloride (CTAC, Tokyo Chem., Inc.), and a nonionic surfactant, hexadecyl polyethylene ether (Brij-56, Aldrich), were used (Figure 1). Tetraethoxysilane (TEOS) was purchased from Kanto Chemical. The chemical structure of the surfactants is shown in Figure 1.

Preparation of the PPLC Film. The PPLC was solved in chloroform as the solvent. The concentration of the polymers in the chloroform solutions was 5 wt %. Films of the polymer were prepared on a quartz or Si substrate by spin-coating of the solutions (first spin, 1000 rpm, 5 s; second spin, 2000 rpm, 30 s). The polymer films were dried at room temperature for 1 day in a darkroom. The thickness of the polymers films was about 70 nm.

Synthesis of Mesoporous Silica Thin Films. The mesostructured surfactant/silica hybrid films were synthesized on the PPLC films (as seen in Figure 2e) by two preparation methods as follows.

Static Deposition Method. TEOS was mixed with CTAC or Brij56 in an HCl/water/ethanol acidic solution, and the mixture was stirred for 3 min at 50 °C. The molar ratios of components in these sol solutions were 0.1:0.11:100:7:4 TEOS/CTAC/H_2O/HCl/EtOH for CTAC and 0.1:0.11:100:3 TEOS/Brij56/H_2O/HCl for Brij56. Mesostructured surfactant/silica hybrid films were synthesized on the photo-aligned PPLC film by immersing in the above precursor sol solutions containing CTAC or Brij56 at 60 °C for 48 h.

Dip-Coating Method. TEOS was mixed with the CTAC acidic water/ethanol solution as described for the method 1, and the mixture was stirred for 3 h at 60 °C. The molar ratio was 1:0.5:6.5:0.04:26−160 TEOS/CTAC/H_2O/HCl/EtOH in this case. The PPLC film on a substrate was immersed into this solution and lifted up at 2 mm/s at a relative humidity of 40−50%.

For removal of the template, the mesostructured CTAC/silica hybrid films were subjected to irradiation with ultraviolet light (185 and 254 nm) under an O_2 atmosphere (i.e., O_3 oxidation process[28]) at room temperature for 1.5 h. For Brij56/silica hybrid films, calcination at 200 °C for 4.5 h followed by the O_3 oxidation was performed.

Photomicropatterning of Mesostructured Silica Films. Patterned photo-orientation to the PPLC film was performed by irradiation through a photomask (3.6 J cm^{-2} at 313 nm), and the film was subsequently annealed at 150 °C. The mesostructured silica film was prepared on such a PPLC film by the static deposition method.

Characterizations of the Mesostructuered Silica Films. The thicknesses of silica hybrid films prepared by the two methods were measured by atomic force microscopy (Nanopics 2100, Seiko Instruments, Inc.).

Morphologies of the films on a quartz plate were observed by optical microscopy (OLYMPUS, BX51).

The Fourier transform infrared (FT-IR) spectra were recorded on a Biorad FTS6000 spectrometer equipped with a DTGS detector. The system was purged with dried air. A silicon wafer was used as the substrate for transmission measurement. The measurement was carried out in the normal incidence.

For the mesoporous silica thin film prepared by the static deposition method, transmission electric microscopic (TEM) images were obtained with a Hitachi HF-2000. The sample for the TEM observation was attached onto a mount by an epoxy resin. The pieces of the silica film were prepared by tearing off from the substrate and polishing to obtain a region of the sample about 30 μm thick.

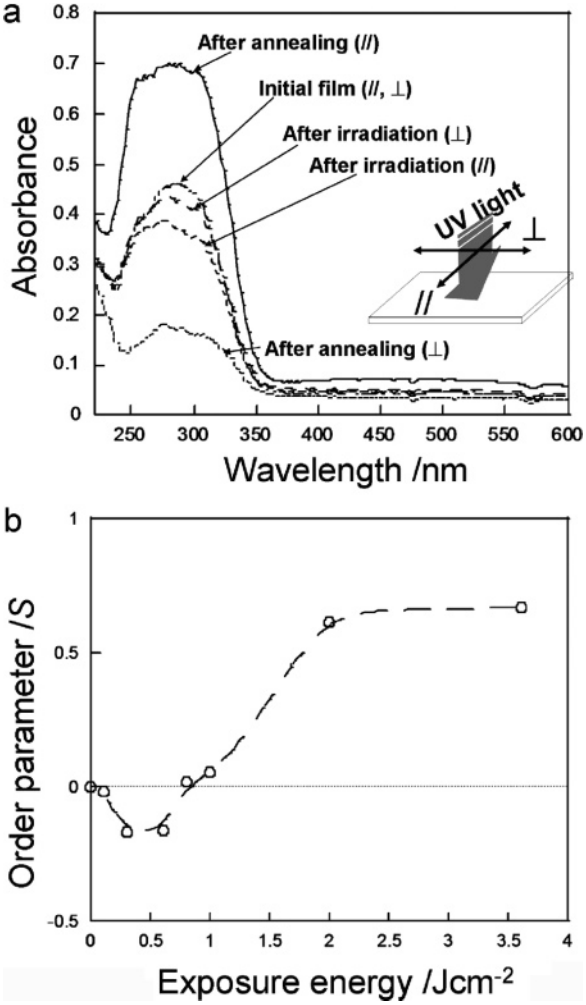

Figure 3. Polarized UV−visible absorption spectra of the PPLC film (a) and in-plane order parameter (*S*) of the PPLC films after exposure of the LPUV light and successive annealing as a function of exposure energy (b).

X-ray diffraction (XRD) patterns of the silica hybrid films and silica powders obtained by crushing the films were performed with a RINT-2100 (Rigaku) and a NanoViewer (Rigaku) using Cu Kα radiation. In-plane XRD measurement for the film was performed on an X-ray diffractometer equipped with a four-axis goniometer (Rigaku, ATX-G) using Cu Kα radiation. Photo-orientation of the mesochannels of the silica films on a silicon wafer was evaluated by this method. The degree of orientation [D.O. (%)] of the mesochannels was calculated by the following equation:[29]

$$\text{D.O.} = \frac{360° - \sum W_i}{360°} \times 100$$

where W_i (deg) is the full-width of degree at half-maximum of the diffraction peak in the in-plane XRD profile, with the subscript *i* being the number of peaks.

Results

Photo-Orientation of the PPLC Film. Polarized UV absorption spectra of the PPLC film are shown in Figure

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3a. When the PPLC film was irradiated with LPUV light, the UV absorbance at 313 nm decreased. A small optical anisotropy ($A_{\parallel} < A_{\perp}$) at 313 nm was induced. This means that the mesogenic side chains (biphenyl and cinnamoyl) whose optical absorption axis was in parallel to the polarized direction of the LPUV light were selectively excited to undergo the photodimerization of the cinnamoyl moiety.

After annealing at 150 °C (liquid crystal region), the anisotropy was largely enhanced ($A_{\parallel} \gg A_{\perp}$). Such amplification of the anisotropy is attributed to the self-assembly of the liquid crystal nature. To describe in detail, after annealing nonreacted mesogenic side chains were aligned following the photo-cross-linked side chains whose absorption axis was fixed in parallel to the polarized direction of the LPUV light (Figure 2d). As a result, absorbance at 285 nm of the biphenyl unit of the side chains showed a large in-plane anisotropy in parallel to the polarized direction of the LPUV light. The order parameter (*S*) of the mesogenic side chains reached 0.6.

S for the PPLC films after annealing changed when the exposure energy of irradiating LPUV light was varied. Figure 3b shows the relation between *S* and the exposure energies. Figure 3b shows the relation between *S* and the exposure energy. *S* became negative in sign at an exposure energy below 1 J cm^{-2}. This indicates that mesogenic side chains were preferentially aligned perpendicular to the polarized direction of the LPUV light. Upon further irradiation, the sign reversed to positive at 1 mJ cm^{-1}; namely, the molecular orientation preferentially becomes parallel to the light polarization. The enhancement of *S* continued until 2 J cm^{-2} to give a saturated value ($S = 0.6$) above this exposure dose. The orientational inversion is attributed to the involvement of two photoreactions of different time constants, that is, fast photoisomerization and slow photodimerization of the cinnamoyl unit.[26] At the earlier stage, the $E-Z$ photoisomerization dominates, providing perpendicular molecular orientation. At the latter stage, in contrast, the parallel-orienting photodimerization preferentially proceeds.

Structural Characterizations of Mesoporous Silica Films. On the above photo-aligned PPLC film, the surfactant-templating silica films were synthesized by both method 1 and method 2. The thickness of the silica films obtained by the static deposition method ranged 300−400 nm. For the dip-coating method, the thickness was changed from 40 to 200 nm by adjusting the content of ethanol from 76 to 33% in the sol solution. The resulting mesoporous silica films synthesized on the polymers were highly transparent. The transmittances at wavelengths in the visible region (400−800 nm) were 91 and 96% for the films prepared with the static deposition method and the dip-coating method, respectively.

To remove the template surfactant, the resulting silica films were subjected to O_3 oxidation or heat calcinations. Figure 4 displays the FT-IR spectra before and after the template removal. As clearly seen, symmetric and asymmetric C−H stretching vibration peaks at 2840−2970 cm^{-1} essentially fully disappeared after the treatment. It is noteworthy that the complete disappearance of the C−H stretching band indicates that not only the pore template (surfactant molecules) but also the alignment template of the PPLC film lying underneath are removed. On the other hand, the Si−O stretching band around 1070 cm^{-1} was essentially unchanged, indicative of the retention of the siloxane network structure.

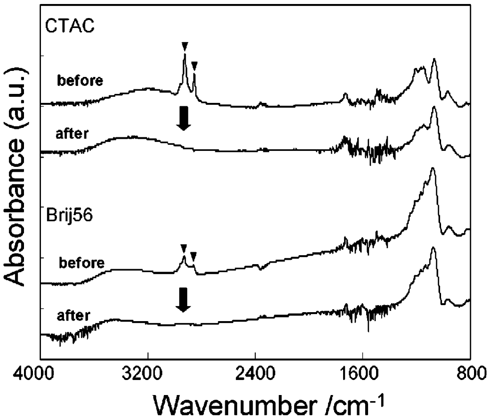

Figure 4. FT-IR spectra of mesostructured silica films obtained by templating of CTAC or Brij56 on the PPLC film, before and after removal of surfactant.

Structural information of the mesostructured silica film prepared by the above methods was provided from XRD measurements (Figure 5).

Figure 5a shows the $\theta-2\theta$ XRD patterns of crushed powders of as-synthesized mesostructured surfactant CTAC/silica hybrid film. Clear diffraction peaks (filled inverted triangles) were observed corresponding to the (100), (110), (200), and (210) diffractions. This result means that the mesostructures of surfactant (CTAC)/silica composites have the 2D-hexagonal packing (*P*6*mm*).

Figure 5b shows the $\theta-2\theta$ XRD patterns for the as-synthesized mesostructured surfactant (CTAC or Brij56)/silica hybrid film (filled inverted triangle) and for the calcinated samples (open inverted triangle).

For the CTAC system, clear diffraction peaks (filled inverted triangles) were observed at $2\theta = 2.54°$ and 5.08° corresponding to the (100) and (200) diffractions of the 2D-hexagonal packing of the mesochannels with $d_{100} = 3.48$ nm. The absence of the (110) and (210) diffraction peaks that were seen in the powder sample (a) indicates that the cylindrical mesochannels are oriented parallel to the plane of the PPLC film.

After removal of the template surfactant (open inverted triangles), the intensity of the XRD peak was retained at a comparable level, and 2θ showed a slight shift to a wider angle ($2\theta = 2.71$ and 5.42° corresponding to the (100) and (200) diffractions, respectively, with $d_{100} = 3.27$ nm).

For the as-synthesized hybrid film that used Brij56, the diffraction peaks (filled inverted triangles) were observed at $2\theta = 1.5$ and 3.0° corresponding to the (100) and (200) diffractions, respectively, of the 2D-hexagonal structure with $d_{100} = 5.9$ nm. Similar to the CTAC system, the absence of the (110) and (210) diffraction peaks is indicative of the parallel orientation of the cylinders to the plane of the PPLC film. After the removal of the template surfacant, the diffraction peaks (open inverted triangles) were observed at $2\theta = 1.9$ and 3.8° corresponding to the (100) and (200) diffractions, respectively. The value of d_{100} is 4.6 nm, indicating that the mesoporous silica film with larger

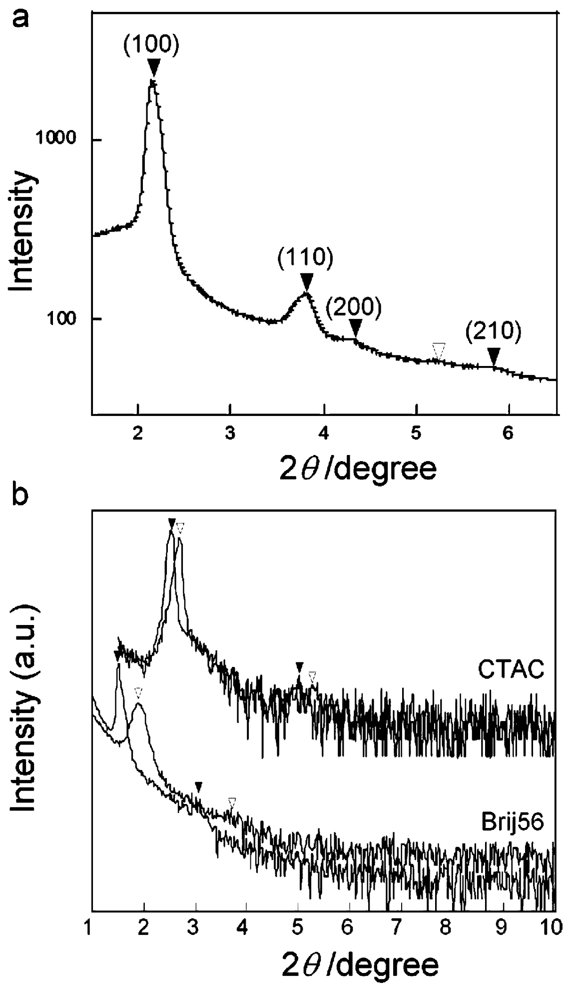

Figure 5. XRD pattern of a powder sample after crushing the mesostructured silica film (a). The peaks of filled inverted triangle correspond to the mesostructured silica. A peak of the open inverted triangle comes from the epoxide resin used to fix the sample. XRD patterns for mesostructured silica thin films obtained by templating of CTAC or Brij56 (b). Filled and open inverted triangles indicate peaks before and after removal of the surfactant, respectively.

mesostructures was obtained. Significant enlargement of the pore size has been also reported by Miyata et al.[30] by replacing the template CTAC with Brij56.

The mesostructure of the mesoporous silica film was directly visualized by TEM observation. Figure 6 shows the TEM image of surface of the mesoporous silica film synthesized with CTAC by the static deposition method. Cylinder alignment of the 2D-hexagonal structure of the mesoporous silica film was clearly observed. This knowledge agrees with the results of the X-ray analyses that the mesochannels are oriented parallel to the plane of the PPLC film. The layer pitch of the magnified image shows the lattice spacing to be about 4 nm, which agrees with the data of the X-ray measurements. This figure also shows that the cylinders are highly aligned in a range of several hundred nanometers at least.

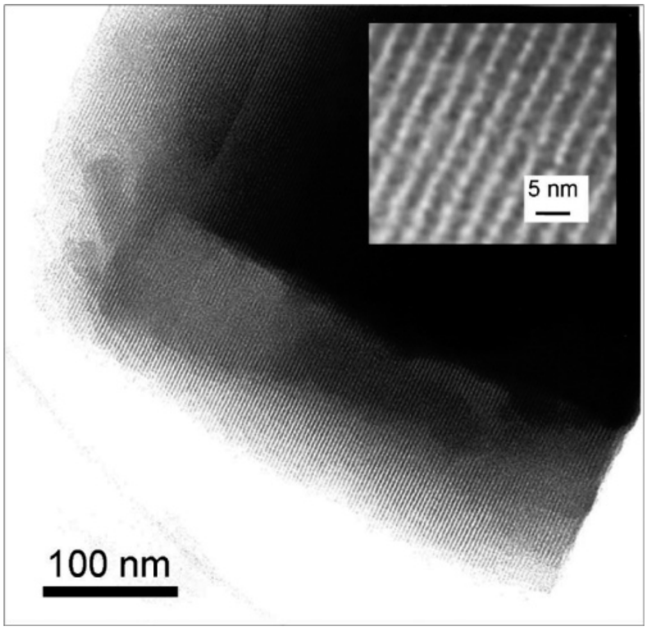

Figure 6. TEM image of the mesoporous silica film.

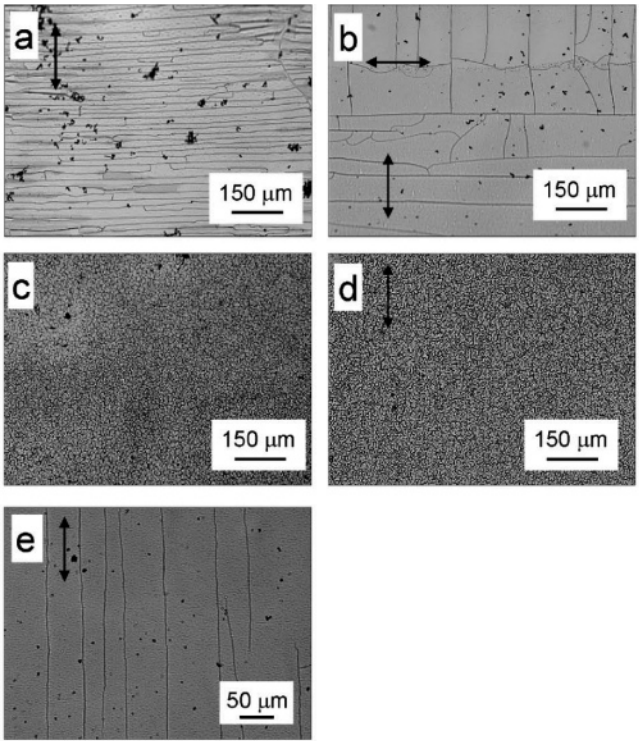

Figure 7. Optical microscopic images of the mesoporous silica films synthesized on the PPLC film by the deposition method. The arrows show the polarization direction of irradiating LPUV light.

In-Plane Photo-Orientation of the Mesoporous Silica Film on PPLC. Morphologies of the surfactant-templated silica composite thin films on the PPLC film obtained by the static deposition method were observed by optical microscopy. Figure 7a−e shows optical microscopic images of the CTAC/silica thin films. In the mesoporous silica film on the photo-aligned PPLC film, straight and uniformly aligned cracks appeared (a). The direction of the cracks was directed perpendicular to the polarized direction of irradiated LPUV light. When irradiation with two polarization directions was performed onto separate areas of a single PPLC film, parallel cracks running in two distinct directions were observed (b). In contrast, such aligned cracks did not appear for a PPLC film irradiated with nonpolarized UV light, and

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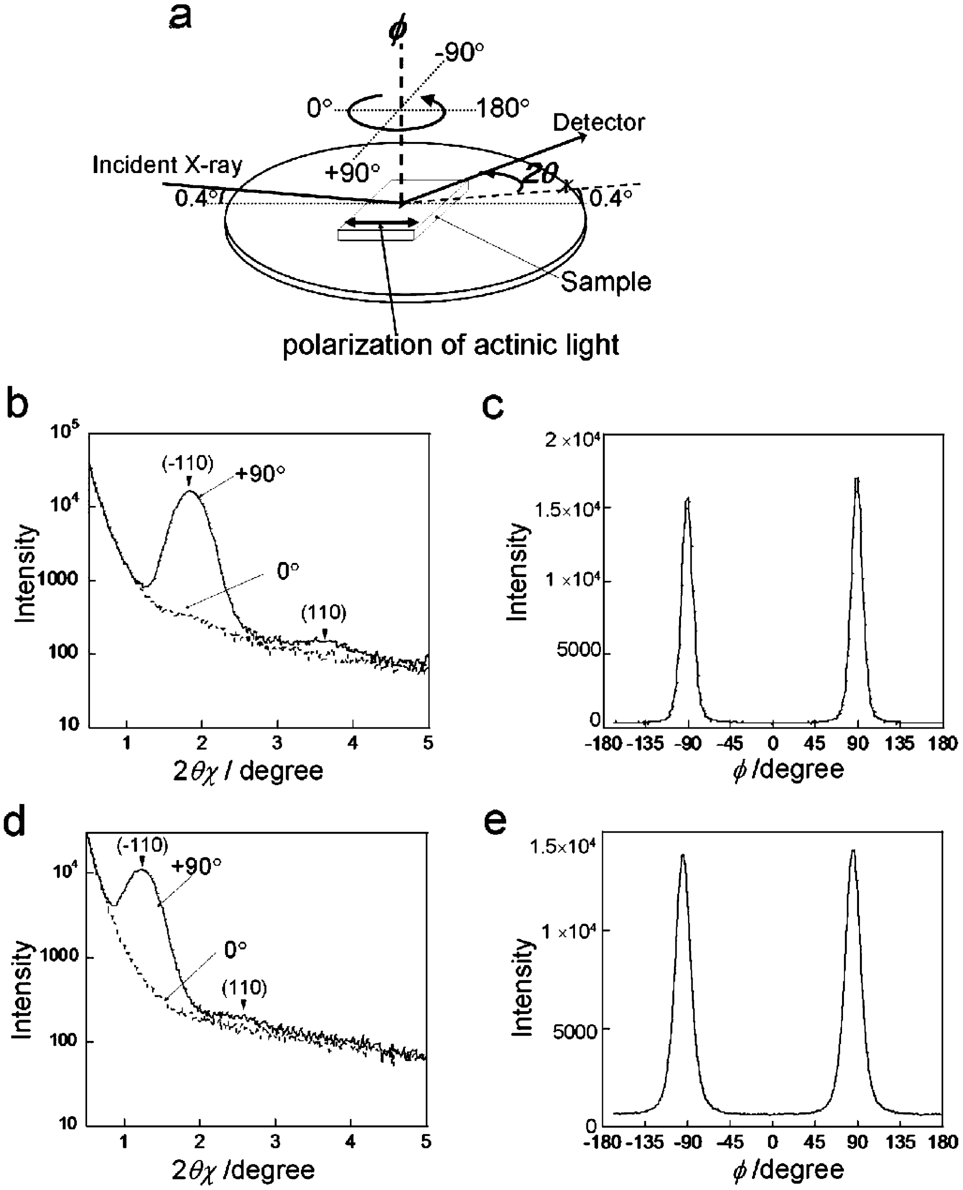

Figure 8. Illustration of the configuration of the in-plane XRD measurement (a). The $\phi - 2\theta_\chi$ XRD scan profiles for the surfactant/silica mesostructured composite film on the PPLC film in the cases of CTAC (b) and Brij56 (d). XRD scan profiles obtained in the in-plane rotation (ϕ) for the composite film on the PPLC film in the cases of CTAC (c) and Brij56 (e).

the silica film shows grain morphologies with no preferred orientations (c). The above results indicate that the linear cracks seen in Figure 7a are produced by an in-plane anisotropic internal stress. Most probably, the existence of macroscopically aligned nanochannels should be attributed to this. Without the annealing process (Figure 2c), uncontrolled grain morphology was also observed (d). Thus, the annealing process of the PPLC that generates a large degree of mesogen orientation is necessary to attain the effective epitaxial orientational transfer to the alignment of surfactant rodlike aggregate templates.

When Brij56 was used as the template, the straight and uniformly aligned cracks were also observed (e). Interestingly in this case, the linear cracks ran parallel to the polarized direction of the irradiated LPUV light, the orthogonal direction of the system of CTAC. This contrasting result suggests that direction of the anisotropic internal stress depends on the surfactant employed.

The orientation of the mesochannels was evaluated by an in-plane XRD measurement in detail. Figure 8a shows the instrumental arrangement for the in-plane XRD measurement. The polarized direction of the LPUV light irradiated to the film coincided with the parallel direction of the incident X-ray at $\phi = 0°$.

Here, the mesochannel structures synthesized in the two methods are evaluated and compared. In-plane XRD profiles of the silica films synthesized by the static deposition are shown in Figures 8 and 9. Figure 10 shows the data for the silica films synthesized by the dip-coating method.

Static Deposition Method. In Figure 8, data obtained for CTAC and Brij56 templates are indicated in parts b and c and parts d and e, respectively.

Figure 8b shows $\phi - 2\theta_\chi$ XRD scan profiles of the as-synthesized mesostructured CTAC/silica composite thin film. At $\phi = 0°$, the $2\theta_\chi$ XRD signal was not observed. When the sample was rotated to $\phi = +90°$, strong diffractions at $2\theta_\chi$

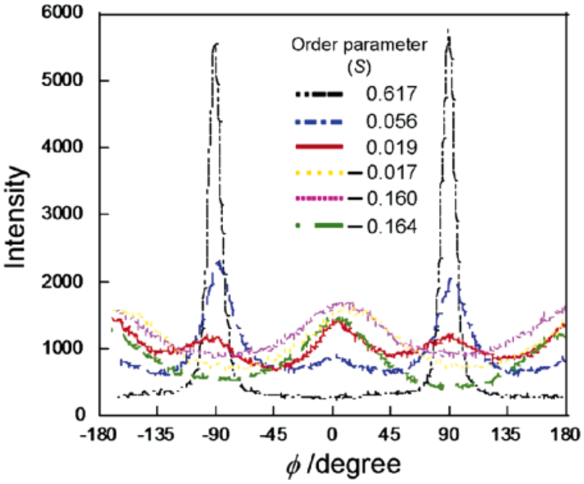

Figure 9. In-plane XRD diffraction profiles of mesostructured composite silica films obtained for samples of various order parameters (S) of side chains of the PPLC films. The samples correspond to the data in Figure 3b.

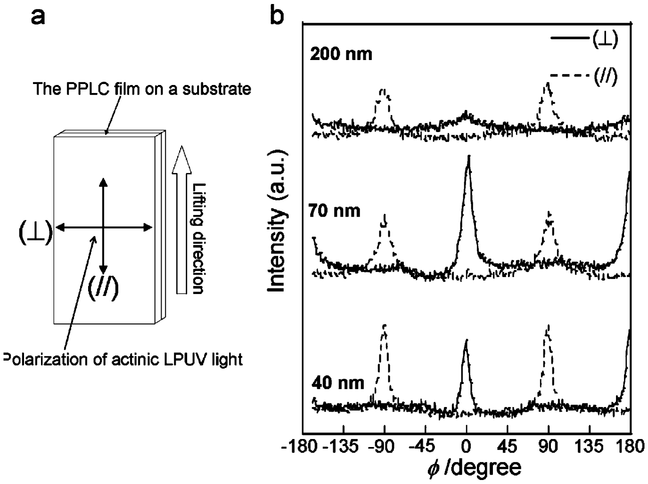

Figure 10. Illustration of the silica film synthesized on the PPLC film by a dip-coating method (a). Two solid arrows in this figure show the polarization directions of the irradiating LPUV light, parallel (||) or perpendicular (⊥) to the dip-coating direction. ϕ-scan in-plane XRD profiles for the surfactant/silica composite films obtained by the dip-coating method (b).

= 1.8 and 3.4−3.8° assignable to the ($\bar{1}10$) and (110) lattice plane perpendicular to the substrate, respectively, were observed (b). These results indicate that the mesochannels are photo-aligned perpendicular to the polarized direction of the irradiated LPUV light. This situation is schematically illustrated in Figure 2e. Next, in-plane rotation (ϕ) of the silica thin film was conducted with retention of $2\theta_\chi = 1.8°$ (c). In the −180 to +180° rotation, two obvious diffraction peaks with very narrow directional distribution were observed at $\phi = -90$ and +90° (c), indicating that the photo-oriented mesochannels have a preferential orientation perpendicular to the polarized direction of the LPUV light. The degree of orientation (D.O.) of the photo-aligned mesochannels reached 92% from the full width (W) of ϕ at half-maximum of the two diffraction peaks. The value means that mesochannels of the silica film were almost completely aligned uniaxially.

The same measurements were performed for the Brij56 template system. Similar to the system of the CTAC template, the diffraction peak of the ($\bar{1}10$) and (110) lattice plane perpendicular to the substrate was obtained at $\phi =$ +90°. $2\theta_\chi$ of the diffraction peaks were observed at 1.2 and 2.3−2.9° in this case (d). The rotation of ϕ also gave two distinct diffraction peaks at $\phi = -90$ and +90°, showing that the channel direction is the same as for the CTAC templating. D.O. was somewhat lowered to 90% in this case.

The silica films were synthesized on the PPLC films with the various degrees of order shown in Figure 3b. Change of the in-plane XRD scan profiles of the silica films was shown in Figure 9. The intensity of the diffraction peaks of the silica film at $\phi = -90°$, +90° decreased, and also D.O. of the mesochannels decreased from 92 to 70%, when S of the PPLC film became lower from $S = 0.617$ to $S = 0.019$. The results of in-plane XRD profiles indicate that the order of photo-alignment of mesochannels is sensitive to the molecular orientation of the underlying PPLC film. High in-plane orientation of the PPLC film ($S \geq 0.6$) was essential for producing high photo-orientation of the mesochannel. We think that this knowledge should be of importance for the design of other alignment layers.

In addition, the diffraction peaks were observed at $\phi = 0$ and ±180°, when S of the PPLC film was negative in sign ($S = -0.07$ to -0.164). This fact indicates that the direction of the mesochannels can be altered by adjusting the exposure dose of LPUV light.

Dip-Coating Method. In Figure 10, in-plane XRD profiles of the CTAC/silica composite films synthesized by the dip-coating are depicted. In the measurements, the direction of incident X-ray at $\phi = 0°$ coincided with the parallel direction of the dip-coat (lifting) direction (see Figure 8a). LPUV light was irradiated on PPLC films in parallel (||) and perpendicular (⊥) to the dip-coating direction as displayed in Figure 10a. In the same manner as that mentioned in the static deposition method, a scan profile of in-plane rotation (ϕ) was obtained at $2\theta_\chi = 1.8°$. In the case that the polarized direction of the irradiated LPUV light was set parallel (||) to the lifting direction, two sharp diffraction peaks were observed at $\phi = -90$ and +90° (b). In contrast, when the polarized direction was set perpendicular (⊥) to the lifting direction, the diffractions were observed at $\phi = 0$ and ±180°. These facts obviously indicate that the mesochannels are aligned to the polarized direction of the LPUV light, which agrees with the result of the static deposition method. It is stressed here that the channel orientation is predominantly controlled by the direction of the photo-aligning polymer layer and not by the lifting direction. This aspect will be discussed later.

The thickness of the silica film was changed by controlling the molar content of ethanol in the sol solution as described in Experimental Section. As the molar concentration of ethanol was lowered, the film became thinner. The orientation degree of the mesochannels was dependent on the thickness of the silica thin film as seen in Figure 10b. The thinnest film (thickness: 40 nm) had the highest order of orientation of the mesochannels, D.O. reached to 93%, both parallel (||) and perpendicular (⊥) to the dip-coating direction. The D.O. values for the film of 70 nm thickness were 92 and 91% in the cases of parallel (||) and perpendicular (⊥) lifting, respectively. The orientational order considerably decreased for the film of 200 nm thickness. The D.O. values reduced to 73 (||) and 91% (⊥). In the above fashion, the effective photo-

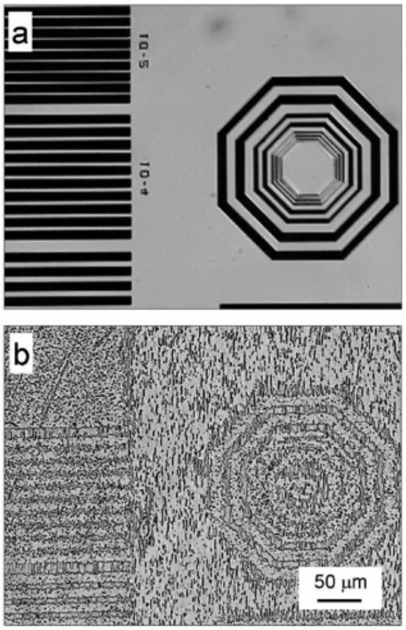

Figure 11. Optical microscopic images of a photomask (a) and mesostructured silica film that is photomicropatterned on the PPLC film by irradiation through this photomask (b). The arrow shows the polarized direction of the irradiating LPUV light.

alignment can be achieved for thinner films. These facts unequivocally indicate that surface-mediated transcription was attained form the molecular orientation of the PPLC film to the surfactant rodlike aggregates.

Photomicropatterning of the Mesochannels. Micropatterned illumination of LPUV light to the PPLC film was achieved, and the morphology of the resulting silica film was observed by optical microscopy (Figure 11). The PPLC film was irradiated with the LPUV light through a photomask and annealed. In the irradiated area with LPUV light, linear cracks evolved whose direction ran perpendicular to the polarized direction of the LPUV light. In contrast, grain morphologies were seen in the unilluminated areas. These morphological features strongly suggest that local alignments of mesochannels were attained in the geometry of the photomask. The patterning resolution in this experiment was about 10 μm.

Discussion

Advantages of the Present Photo-Alignment Method. Our previous work[19,20] utilized the photoisomerization of the azobenzene-containing layer for photo-alignment of mesoporous silica. The former process involves two transfer steps, transfer from a photo-oriented azobenzene monolayer to a polysilane film and that from the polymer film to the mesostructured silica. We point out here that the procedure using the photodimerization of PPLC mentioned in this paper is advantageous in two aspects, simplicity of the process and structural stability. The simplification of the process is of no doubt. The present method consists of only a one-step transfer and requires little skill in the experiments. We will touch on some merits of the stability increase of the mesopore structure.

$\theta-2\theta$ XRD profiles in Figure 5b show that the 2D-hexagonal structure is hardly damaged after calcination processes for template removal, as indicated by the comparable intense peak even after the template removal. In the previous method, the peak intensity was reduced to about one-fifth of the original after the template removal (see Figure 5 of ref 20). The significant improvement of the structural stability is ascribed to achievement of siloxane condensation at higher temperatures (50−60 °C) where sufficient network formation occurs. In the previous method using the polysilane film, the reaction temperature is limited to lower temperatures below 40 °C, practically to room temperature, because the polysilane film readily loses the orientation above this temperature. Therefore, the network formation is insufficient. In the present system utilizing the dimerization process, the alignment film becomes even more stable by cross-linking.

The stability improvement of the mesostructure then lead to superior alignment quality of the mesochannels, higher resolution in the micropatterning, and better optical quality of the resulting film. D.O. of the mesochannels reaches 92%, whereas that prepared by the previous azobenzene polymer monolayer/polysilane layer is smaller (87% as calculated from the X-ray data shown in Figure 2 and Figure 5 of refs 19 and 20). The resolution obtained here (10 μm, Figure 11) is much better than that obtained in the oriented azobenzene/polysilane system (typically above 100 μm[20]). The stabilized structure resists formation of macroscopic cracks providing transparent silica films. Light scattering due to the surface roughness is highly suppressed in this work (see Figure 3 of ref 20 for comparison).

On the Selection of Template Surfactant. In general, cationic and nonionic surfactants are used as templates for the synthesis of mesoprous silica. As indicated here, both cationic and nonionic surfactants are applicable for the surface mediated photo-alignment. The in-plane orientational order is satisfactorily high as to give D.O. = 92 and 90%. The size and features of the mesostructure are dependent on the structure of the surfactant. Variations of mesopore size will be an interesting subject to pursue because there are a number of research objectives and functional molecules or materials to be incorporated. CTAC and Brij56 provide pore diameters of ca. 3 and 5 nm, respectively, and thus the variation of the pore size is attained at this level. We regard that the photo-aligned mesostructures with larger size with templating of Brij56 will be more useful for incorporation of optically and electronically active functional materials. Work in this regard is now in progress. The direction of macroscopic crack formation in the photo-aligned mesostructured silica film is reversed between CTAC and Brij56, and the linear cracks run parallel and orthogonal to the channel direction for CTAC and Brij56, respectively. This is an interesting observation; however, this discrepancy cannot be explained yet.

Even larger mesostructures can be synthesized by templating a nonionic block copolymer surfactant consisting of poly(oxyethylene) and poly(oxypropylene) chains called P123.[31,32] The diameter of the mesopore will be about 10 nm in this case, which will be suitable for larger molecules

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or nanoparticles incorporation. In this context, we have also made an attempt using P123; however, photo-alignment of the mesochannels at large scales was found to be unsuccessful. Probably, this is due to formation of a rather ambiguous aggregate of this block copolymer (as seen in the TEM image of ref 33).

Features of the Dip-Coating Method. The dip-coating method is particularly useful as a versatile and practical technique for the fabrication of mesostructured surfactant/silica thin films because of its facile procedure and uniformity of the resulting film.[34] Previous investigations have shown that the mesochannels are aligned in the lifting direction because of a mechanical flow factor when prepared on an unmodified plane surface. Contrary to our expectation, the mesochannels are definitely aligned only along the photo-aligning direction of the PPLC film. In other words, the channels are not oriented to the flow direction of the sol solution (Figure 10b). The surface-mediated aligning power surpasses the flow orientation. Miyata and Kuroda have very recently found the same effects for the rubbed polyimide surfaces.[16]

In the dipping method, the solvent is much more rapidly evaporated, which may possibly lead to structures different from those obtained by the static deposition. With regard to pore size and structural features, we did not admit a significant difference between the two preparative methods of the static deposition and dipping methods as far as CTAC was employed as the template. This will provide a great merit that patterning of the mesochannels by patterned or site-selective irradiation is readily performed by the simple dipping method. We anticipate that more extended applications utilizing photo-aligned mesochannels will be feasible due to its simple and less laborious procedures.

Conclusions

We succeeded in photo-alignment of the 2D-hexagonal (*P*6*mm*) mesopores in the silica thin film via epitaxial transfer from a PPLC film. The in-plane XRD measurements revealed that the mesochannels of the silica film are aligned perpendicular to the polarized direction of the LPUV light irradiated onto the PPLC film. On the basis of the feature of surface morphologies of the silica film, the photo-alignment is performed at the macroscopic scale areas in the entire area of irradiation. In addition, on-demand micropatterning of the photo-aligned mesoporous silica films can be readily attained at a resolution of about 10 μm by irradiation through a photomask. We expect that development of the photo-alignment technique of the mesoporous silica film will provide new opportunities for fabrication of organic–inorganic hybrid materials and devices for optoelectrical uses.

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