

Synthesis of Photo-aligned Mesoporous Silica Thin Films on Photo-crosslinkable Polymer Film

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Mesoporous silica thin films with aligned mesochannels in one direction at large scales will be applied in optics, electronics, separation technologies etc. We propose herein a new photo-aligning and micro-patterning technique for mesochannels of a silica thin film using a photo-crosslinkable polymer film with a cinnamoyl group. The polymer film was uniaxially oriented by exposure to linearly polarized light (LPL). On the film, a mesoporous silica thin film was synthesized. The orientation of the mesochannels was evaluated by in-plane XRD measurements. It was shown that the mesochannels were aligned parallel to the polarized direction of the irradiated LPL.

Key words: Mesoporous silica thin film, photo-crosslinkable polymer film, linearly polarized light, Photo-alignment

1. INTRODUCTION

Mesoporous materials such as MCM-41^[1] and FSM-16^[2] synthesized via templating of organic surfactant aggregates possess large surface area and uniformly sized pores (typically 2 – 10 nm diameter) mostly arranged in two-dimensional hexagonal arrays. These materials have attracted increasing attention as catalysts for larger molecules and also for creation of various functions such as separations, chemical sensing of molecules^[3]. Thin films of mesoporous silica can be prepared by spincoating,^[4] dip-coating^[5] and deposition method^[6,7]. The thin films prepared in above manners possess aligned mesochannels at local levels; however they are randomized at larger scales when deposited on an untreated flat substrate. Development of alignment methods of mesochannels in one direction at larger scales are anticipated to find many attractive applications in optics, electronics, separation technologies etc. However, only a few attempts are made so far. One practical alignment method can be an orientational transfer from a surface of an oriented polymer film as widely applied in liquid crystal alignment technology. In fact, deposition on a rubbed surface^[10] of polyimides can be used for orientation of mesochannels. Nevertheless, such 'mechanical' procedures will be applied to limited use, and fabrication of devices possessing oriented nano-spaces will require on-demand controls of locally addressed orientations and micropatterning.

Photoalignment technique^[8,9] can be an attractive alternative in this regard. We have previously attained photo-controls and micro-patterning of mesochannels of

a silica thin film using a photo-orientation process of an azobenzene polymer monolayer^[10]. However, the above photoalignment system based on the photoisomerization of azobenzene has some drawbacks from practical viewpoints as follows. The process is complicated and demands handling skills, therefore the structure of channels were not stable due to insufficient the siloxane condensation.

To overcome above problems, we propose herein a new versatile photoalignment technique using a photo-crosslinkable side-chain-type polymer liquid crystal (PPLC). We employed poly[6-(4-(4'-methoxycinnamoyloxy)biphenyloxy)hexylmethacrylate] as the PPLC in which the mesogenic biphenyl group is combined with a photo-crosslinkable cinnamoyl terminal (Figure 1a). In this PPLC film, the anisotropy of angular selective [2 + 2] photodimerization between two cinnamoyl units proceeded by linearly polarized UV (LPUV) light is largely amplified by the directly linked mesogenic biphenyl moiety through the liquid crystalline nature. The PPLC film itself can be applied for fabrication of optical memory devices, retardation films, photoalignment layer for a liquid crystal orientation^[11]. Another advantage to use PPLC is that the resultant photochemical crosslinking firmly fixes the molecular orientation. This will lead to facile performance of siloxane condensation at higher temperatures without damaging the film.

2. EXPERIMENTAL

2.1. Photo-orientation of Photo-crosslinkable Liquid Crystal Polymer Films

The photo-crosslinkable liquid crystal polymer (PPLC) film was synthesized according to the method described in the literature^[12]. The number-average molecular weight (M_n) was about 8.7×10^4 , $M_w/M_n = 2.0$. The polymer melts at 120°C , showing a nematic LC phase, and decomposes at 320°C .

The photo-orientation process of the PPLC film is schematically indicated in Figure 1. First, the spincoated film of PPLC film was prepared. The mesogens had random orientations at this stage. Irradiation of the LPUV light (3.6 J cm^{-2} at 313 nm) to the polymer film induced a slight preferred orientation of mesogenic side chains whose optical absorption axis was in parallel to the polarization direction of the LPUV light (Figure 1b). Next, the film was annealed at the liquid crystal phase temperature (150°C). This procedure induced a higher orientation of mesogenic side chains in parallel to the polarization direction of the LPUV light (Figure 1c). Finally, irradiation of the polarized or non-polarized UV light (1.8 J cm^{-2} at 313 nm) to the PPLC film was performed. The unreacted cinnamoyl units underwent the photocrosslinking, and thus the orientation of mesogenic side chains were strongly fixed.

2.2. Synthesis of Mesoporous Silica Thin Films on Photo-crosslinkable Liquid Crystal Polymer Films

The mesostructured surfactant/silica hybrid films were synthesized on the PPLC films (as seen in Figure 1d) by two preparation methods as follows.

(1) Static deposition method: Tetraethoxysilane (TEOS) was mixed with an acidic cationic surfactant hexadecyltrimethyl ammonium chloride (CTACl) water/ethanol solution, and the mixture was stirred for 3 min at 30°C . A molar ratio of components in the sol solution was 1TEOS : 1CTACl : $1000\text{H}_2\text{O}$: 70HCl : $0-40\text{EtOH}$. A mesostructured surfactant/silica hybrid film was synthesized on the photo-aligned PPLC film by immersing in the precursor sol solution containing CTACl as the template surfactant at 50°C for 48 h.

(2) Dip-coating method: TEOS was mixed with CTACl 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 1TEOS : 0.5CTACl : $50\text{H}_2\text{O}$: 0.04HCl : $26-160\text{EtOH}$. A surfactant/silica hybrid film on a PPLC film was dip-coated at 2 mm/s in a case satisfied with a moisture of humidity (40-50 %). The thickness of silica hybrid films was measured by atomic force microscopy (Nanopics 2100, Seiko Instruments.Inc).

For removal of the template, mesostructured surfactant/silica hybrid films prepared by each method were irradiated with ultraviolet light (185 and 254 nm) at room temperature for 1 h under O_2 atmosphere (i.e. O_3 oxidation process), the mesoporous silica thin films were obtained. The removal of the template surfactant was confirmed by a disappearance of

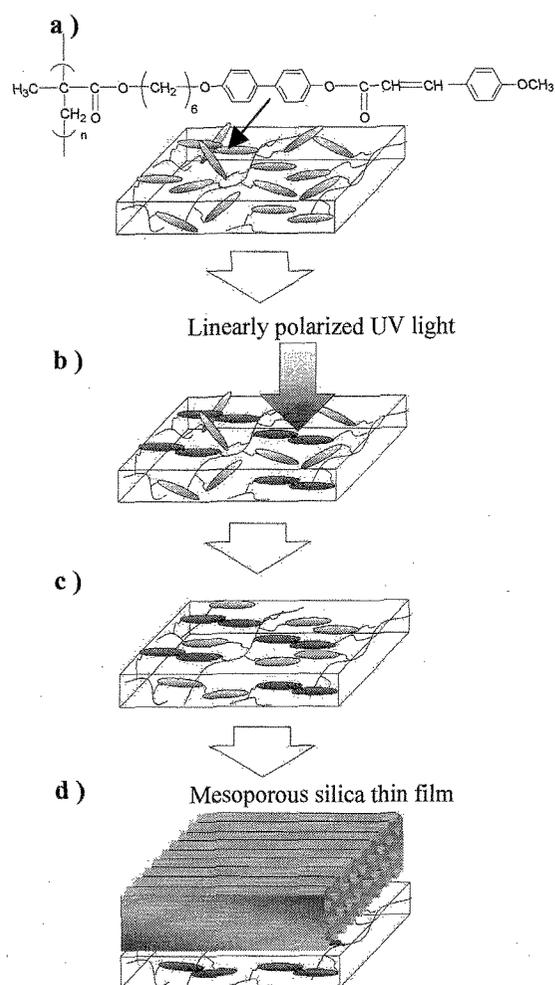


Figure 1. Chemical structure of PPLC and Photo alignment procedure of the PPLC spincoated film.

C-H stretching vibration peak at $2840-2970 \text{ cm}^{-1}$ in FT-IR spectroscopy (Biorad FTS6000).

XRD patterns were taken on a RINT-2100 (Rigaku) using CuK_α radiation. In-plane XRD measurement was performed on an ATX-G (Rigaku) using CuK_α radiation.

3. RESULTS AND DISCUSSION

The mesoporous silica films synthesized by both methods were highly transparent. In addition, a surface of the silica films obtained by the dip-coating (2) became very flat. Thickness of the silica films obtained by the static deposition method (1) was about $300-400 \text{ nm}$. The silica films obtained by the dip-coating (2) was $70-300 \text{ nm}$.

X-ray diffraction (XRD) measurements provide conclusive structural information. (as seen in Figure 2) Figure 2 shows the XRD patterns of the as-synthesized mesostructured surfactant/silica hybrid film (black inverted triangle) and the mesoporous silica film after removal of the surfactant template (white inverted triangle). For the as-synthesized hybrid film, a clear diffraction peak was observed at $2\theta = 2.54, 5.08$

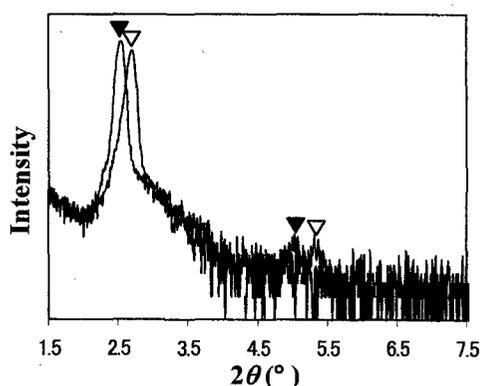


Figure 2. XRD patterns for the mesostructured silica films on the PPLC film \blacktriangledown : as-synthesized; ∇ : after removal of the organic surfactant. The inset shows magnified XRD reflection profiles at $2\theta = 1.5 - 7.5^\circ$.

corresponding to (100), (200) diffraction of the 2D-hexagonal packing of the mesochannels with $d_{100} = 3.48$ nm. This means that the center to center distance of the channel is 4.0 nm. The absence of the (110) and (210) diffraction peaks in these XRD pattern indicates that the mesochannels are oriented parallel to the plane of the PPLC film^[6].

After removal of the template surfactant (white inverted triangle), intensity of the XRD peak was

retained at a comparable level, and the 2θ showed a slight shift to a wider angle ($2\theta = 2.71, 5.42$ corresponding to (100), (200) diffraction, $d_{100} = 3.27$ nm, center to center distance of 3.8 nm). These results indicate that the hexagonal structure of the mesoporous silica film was maintained even after the removal of the template with a slight contraction of the channel diameter. The comparable peak intensity after the template removal is worth mentioning. Our previous attempt with the photo-oriented azobenzene monolayer indicated that the peak intensity reduced to ca. one fifth of the original in the process of template removal^[10]. The significant improvement of the structural stability should be ascribed to achievement of siloxane condensation at higher temperature (50°C) where sufficient network formation proceeds.

The orientation of the mesochannels was evaluated by an in-plane XRD measurement as shown in Figure 3a. A scan of in-plane rotation (ϕ) of the silica thin film synthesized by the static deposition method was conducted at (110) diffraction of the surface structure. In this configuration, $\phi = 0^\circ$ coincided with the parallel direction of the actinic LPUV light. Two obvious diffraction peaks were observed at $\phi = -90$ and $+90^\circ$ as shown in Figure 3b. This result shows that the photo-oriented mesochannels have a preferential orientation in parallel to the polarized direction of the

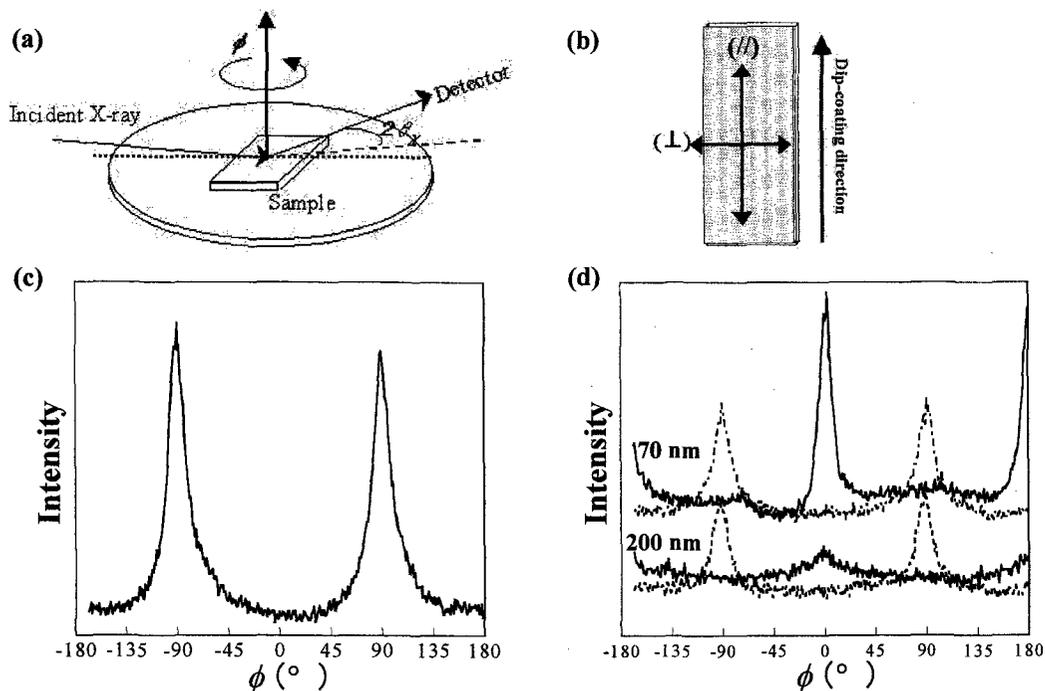


Figure 3. (a) Illustration of the in-plane XRD measurement. (b) The ϕ scan profile of in-plane XRD for the as-synthesized mesostructured silica film on the PPLC film by a static deposition method. (c) Illustration of the silica film synthesized on the PPLC film by a dip-coating method. Two arrows show that the polarized direction of the irradiated LPUV light is parallel(//) or perpendicular(\perp) to the dip-coating direction. (d) The ϕ scan profile of in-plane XRD for the as-synthesized mesostructured silica film on the PPLC film obtained by the dip-coating method.

irradiated LPUV light over the whole plane. The diffraction peaks were sharper and the intensities were higher in comparison with the previous data using azobenzene polymer monolayer^[10]. This indicates that mesochannels of the silica film synthesized on the PPLC film have a higher orientational order than that obtained with an azobenzene monolayer.

In the same way, the orientation of mesochannels of the silica thin film synthesized by the dip-coating method was evaluated. $\phi = 0^\circ$ coincided with the parallel direction of the dip-coating direction (Figure 3c). As seen in Figure 3d, two sharp diffraction peaks were observed at $\phi = -90^\circ$ and $+90^\circ$ in a case that the polarized direction of the irradiated LPUV light was set parallel (*//*) to the dip-coating direction. In contrast, diffractions were observed at $\phi = 0^\circ$ and $\pm 180^\circ$ in a case that the polarized direction was perpendicular (\perp). A previous papers reports that mesochannels of the silica film synthesized by the dip-coating method have a orientation in parallel to the dip-coating direction^[5]. However, our present results lead to an important conclusion that the channel direction is determined by the direction of polarized light (orientation of the underlying polymer film) and not by the dipping direction of the preparative process.

A thickness of the silica film synthesized by the dip-coating could be changed from 70 to 300 nm by changing a molar concentration of ethanol in the sol solution. As the molar concentration of ethanol was lower, the film became thinner. The orientation of mesochannels was dependent on the thickness of the silica thin film as seen in Figure 3d. The intensity of the (110) diffraction peak showed a large variation depending on the film thickness. The film with 70 nm thickness gave more intense diffraction peaks, indicating that the orientation order is reduced as the thickness increased.

Comparisons of the film quality obtained by the two preparative methods are worth mentioning. The silica thin film obtained by the dip-coating was more flat and transparent. Such high quality film may be preferably applied for fabrication of sensitive optical nano-devices.

4. CONCLUSION

We succeeded in photoalignment of the 2D hexagonal channels of mesoporous silica via transfer from a photo-oriented crosslinkable liquid crystalline polymer film. From in-plane XRD measurements, it is concluded that the mesochannels in the film are aligned parallel to the photo-oriented biphenyl mesogens of PPLC. We present here a new finding that, in the dip-coating process, the channel direction is not controlled by the gravitational force in dipping process but by the orientation of the aligning film on the substrate, suggestive of the strong influence of the surface aligning

layer.

A versatile photoaligning method of mesoporous materials is newly proposed using a photo-crosslinkable LC polymer (PPLC) film containing a cinnamoyl unit. When compared with the previous photoaligning process using a photoisomerizable azobenzene layer^[10], marked practical improvements are attained in the two aspects: i) simplification of the process and ii) stability, and thus the quality and transparent property of the resultant mesoporous silica films. Such great improvements are of particular importance for fabrication of optical devices based on incorporation of functional dyes or metal clusters into the mesochannels. We anticipate that the method presented here will find new opportunities of application in mesoporous materials.

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REFERENCES

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature*, **359**, 710(1992).
- [2] S. Inagaki, Y. Fukushima, K. Kuroda, *J.Chem. Soc., Chem. Commun.*, **680**(1993).
- [3] A. Stein, B.J. Melde, R.C. Schrodin, *Adv. Mater.*, **12**, 1403(1997).
- [4] M. Ogawa, *J.Am.Chem. Soc.*, **116**, 7941(1994).
- [5] Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, C. J. Brinker, W. Gong, Y. Guo, H. Soyeyz, B. Dunn, M. H. Huang and J. I. Zink, *Nature*, **389**, 364(1997).
- [6] H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, G.A. Ozin, *Nature*, **379**, 703(1996).
- [7] H. Miyata, K. Kuroda, *Chem. Mater.*, **11**, 1609 (1999).
- [8] K. Ichimura, *Chem. Rev.*, **100**, 1847(2000).
- [9] T. Seki, *Polymer Journal*, **36**, 435(2004).
- [10] Y. Kawashima, M. Nakagawa, K. Ichimura, T. Seki, *J. Mater. Chem.*, **14**, 328(2004).
- [11] N. Kawatsuki, T. Kawakami, T. Yamamoto, *Adv. Mater.*, **13**, 1337(2001).
- [12] N. Kawatsuki, H. Fukumoto, O. Takeuchi, N. Furuso, T. Yamamoto, *Polymer*, **45**, 2615(2004).

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