In situ Polymerization of Liquid Crystalline Monomers within Photoaligned Mesoporous Silica Thin Film

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Photopolymerization of liquid crystalline monomers was achieved within photoaligned mesoporous silica film. After resolving the template of silica networks, bundles of nanofibers containing polymer chains with a narrow molecular weight distribution were obtained.

Mesoporous materials such as MCM-41[1] and FSM-16[2] are synthesized through self-assembly of surfactant, and have large surface area and uniformly sized pores (typically 2–10 nm diameter) mostly arranged in 2D-hexagonal arrays. Such well-defined nanostructures have attracted increasing attention for applications such as catalysts, separations, chemical sensing of molecules, and polymer synthesis.[3] When mesoporous silica is used as a mold of polymer synthesis, the obtained polymers have characteristic properties deviated from those obtained by ordinary bulk or solution polymerizations.[4–7] To date polymers synthesized within the mesopores have been poorly characterized because most of them are conductive polymers and insoluble in solvents. Furthermore, no precise information such as the molecular orientation in the mesopores and the morphologies of the products are reported since only powdered mesoporous silica materials are used for this purpose. It is anticipated that such knowledge will be obtained when the polymerization is achieved in aligned mesoporous silica film at large area scales.

We have recently reported the method for uniform photoalignment of the mesochannels of silica thin film by depositing onto a photocrosslinkable liquid-crystal polymer (PPLC,[8,12] Figure 1a) film oriented by irradiation with linearly polarized UV (LPUV) light.[9] In the deposited silica film, the mesochannels are highly aligned over the irradiated macroscopic area. In the above context, it seemed that performance of radical photopolymerization within the photoaligned mesochannels should be of great value. This letter paper reports on the procedures of this new attempt and detailed characterizations of the obtained polymer products by spectroscopic and microscopic observations.

The photopolymerizable monomers used in this work are shown in Figure 1b. The monomers consist of a mixture of UV curable liquid-crystal (LC) molecules. It was anticipated that the monomers align uniaxially by the liquid-crystal nature in the channels, and that the resulting polymer provides information on molecular orientation. Moreover, the packing state of monomers will be retained during the polymerization for these monomers,[10,11] which should be of help for evaluation of molecular orientation and morphological observations.

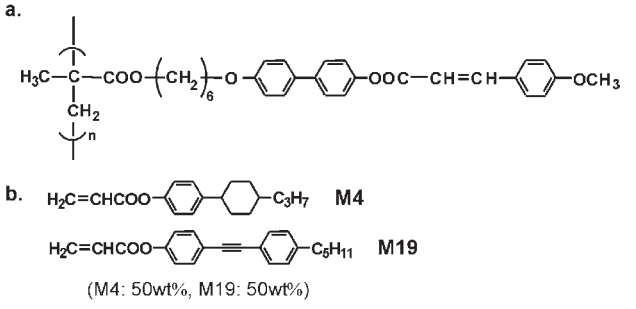

Figure 1. Chemical structure of PPLC (a) and the UV-curable LC molecules (b).

The synthetic procedure of PPLC was described previously.[12] The PPLC film was spin-coated on a quartz substrate from a chloroform solution to give a thin film of 70 nm thickness. Mesogenic biphenyl side chains of this polymer were aligned in parallel to the polarization direction of irradiating LPUV light.[8,12] On the aligned PPLC film, mesoporous silica films were synthesized by a sol–gel reaction of tetraethoxysilane (TEOS) mixed with a cationic surfactant $C_{16}H_{33}N(CH_3)_3Cl$ as the pore template under acidic conditions.[9] A surfactant/silica mesostructured composite film was formed in 2D-hexagonal structure orienting parallel to the plane of the substrate. The thickness of the mesostructured composite silica films ranged 300–400 nm. The pore diameter was ca. 3–4 nm as revealed from X-ray diffraction (XRD) profiles and transmission electron microscopic image. The in-plane XRD measurements showed that the mesochannels were aligned perpendicular to the polarization direction of LPUV light with high orientational order.[9] The mesoporous silica thin film was obtained by removal of templating surfactant and underlying PPLC film through irradiation of ultraviolet light (185 and 245 nm) under O_2 atmosphere (i.e. O_3 oxidation process[13]) for 1 h at room temperature.

The photoaligned mesoporous silica film synthesized as above was exposed to a vapor of 1,1,1,3,3,3-hexamethyldisilazane for 1 day, to produce hydrophobized channel walls. This procedure was required for efficient introduction of hydrophobic monomers into the channels. A photoinitiator, 2,2-dimethoxy-2-phenylacetophenone was added to the liquid of UV-curable LC monomers (0.4 wt % by weight). The LC monomers with the photoinitiator were inserted into the hydrophobized mesochannels at 40 °C for 12 h under a reduced pressure. After incubation at 40 °C for 3 days, the monomer liquid left on the film surface was blown off with a nitrogen gas gun. In situ photopolymerization of the LC monomer was achieved by irradiation with UV light (6 J/cm^2 at 365 nm). Unpolymerized monomers on the surface of the silica film were removed by washing the film with ethanol several times.

Figure 2a shows polarized optical microscopic images of surface for the silica film after the in situ photopolymerization placed between two crossed polarizers. Straight cracks running parallel with each other were observed. This is attributed to the existence of uniaxially photoaligned mesochannels in the silica film as described in Ref. 9. When the silica film was rotated from 0 to 45° in plane, the dark image changed to brighter ex-

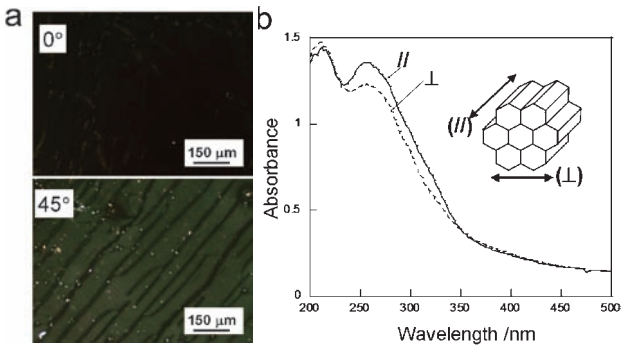

Figure 2. Polarized optical microscopic images (a) and polarized UV–visible absorption spectra (b) of the mesoporous silica film after photopolymerization of LC monomers in the mesochannels.

cept for the crack areas. This indicates that mesogenic moieties of the molecules polymerized in the mesochannels were aligned in one-axis direction. Polarized UV absorption spectra of this film are shown in Figure 2b. The peak at 256 nm corresponds to the absorption band of the mesogens within the mesoporous silica film. $A_{\perp}$ and $A_{//}$ denote absorbance at λ_{max} (=256 nm) observed in perpendicular and parallel to the orientational direction of the mesochannels. In this band, some optical anisotropy ($A_{//} > A_{\perp}$) was induced. The degree of the anisotropy expressed as the dichroic ratio [DR, $DR = (A_{//} - A_{\perp})/(A_{//} + A_{\perp})$] was 0.05. This means that optical absorption axis of mesogenic unit was aligned preferentially parallel to the mesochannels of the silica film. The features of the polarized spectra before and after photopolymerization was essentially unchanged, indicating that the orientation and the packing state of LC molecules was fixed without appreciable change after polymerization.

To extract the polymer products from the channels, the silica network was dissolved by soaking the composite into hydrofluoric acid (HF)/ammonium fluoride buffer solution. The removal of the silica network after the HF treatment was confirmed by FT-IR spectroscopy using a silicon wafer as the substrate. The Si–O stretching vibration band peaking at 1070 cm^{-1} disappeared after the treatment (Figure 3a). On the other hand, the C–H stretching vibration peak at 2800–2900 cm^{-1} remained without damage, indicating that the polymer existed on the substrate. The morphologies of the resulting polymer product were observed by atomic force microscopy (AFM) (Figure 3b). Straight bundles of nanofibers were observed. The height profile of the bundle exhibited the existence of nanometer-scale steps, strongly suggesting the formation of nanofibers by templating the mesopores of 3–4 nm diameter. Seemingly, the retention of the monomer packing during the polymerization of UV-curable LC material[10,11] led to the facile formation of the fibers.

The polymer nanofibers obtained above were dissolved in tetrahydrofuran, and the polymerization behavior was evaluated by gel permeation chromatography. For the polymer synthesized within the mesopores, the number averaged molecular weight (M_n) was found to be 2.3×10^5 with a narrow molecular weight dispersity (M_w/M_n) of 1.3. In contrast, the polymer obtained by the bulk photopolymerization gave the values of $M_n = 1.7 \times 10^5$ and $M_w/M_n = 5.4$. Thus, the molecular weight control is effectively attained by nanolevel caged spaces and the distribution of the polymer synthesized within the mesochannel became markedly narrower.

In conclusion, we succeeded in the in situ photopolymerization of UV-curable LC molecules within the highly aligned mesochannels. After the removal of silica networks, the remaining polymer was obtained as bundles of nanofibers. A particular feature is the homogeneity of the molecular weight of the obtained polymer. We expect that this method can be applied to many other types of monomers, which should be of great technological significance in polymer research.

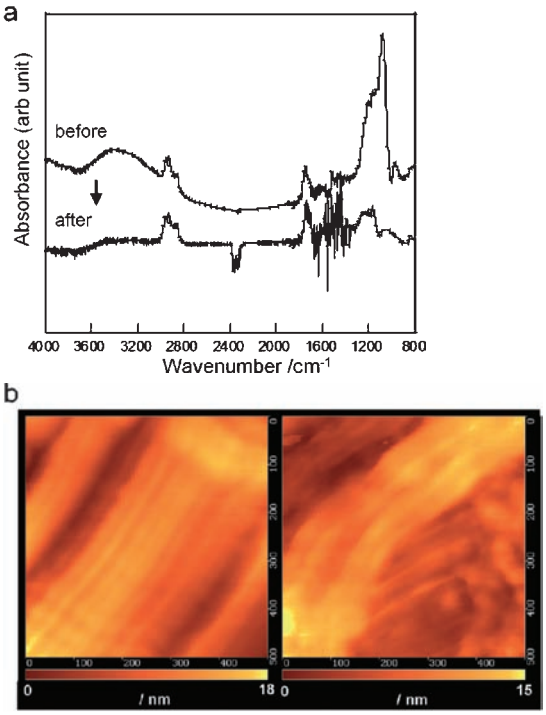

Figure 3. FT-IR spectra of the mesoporous silica film containing the photopolymerized product before and after HF treatment (a). Two AFM images ($500 \times 500\ nm^2$) of the remaining polymer product on the substrate after HF treatment taken at different positions of the film (b).

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