Photo-Orientation of a Mesostructured Surfactant/Silica Hybrid by an Azobenzene Monolayer

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The surface-mediated photoalignment by a photoresponsive molecular layer or polymer film has now become a widely utilized technology in liquid crystal systems. This paper describes our preliminary attempts to align meso-structured silica that are synthesized through supramolecular templating of surfactants. The azobenzene (Az)-containing polymer monolayer was first irradiated with linearly polarized light (LPL), resulting in a photo-orientation of the Az side chain array on the substrate. The first attempt for the direct orientational transfer from this monolayer to the meso-structured material was unsuccessful because the inscribed orientation was completely erased under the conditions required for the sol-gel process of silica synthesis. A successful alignment was achieved through a two-step transfer involving the orientational fixation by a polysilane film followed by the synthesis of silica/surfactant hybrid.
Key words: mesostructured silica, azobenzene, photo-orientation, linearly polarized light

1. INTRODUCTION

Mesostructured inorganic materials, such as MCM-41,[1,2] which are obtained by templating of organic surfactant assemblies possess large surface area and uniformly sized pores. They are more effective than crystalline zeolite molecular sieves as catalysis for larger molecules. Beside simple catalysis, mesostructured materials also have attracted attention in optical materials,[3,4] separations, chemical sensing of molecules,[5] molds of polymers[6] and noble metal wires.[7] The mesochannels may be highly directional at local levels, however they are randomized at larger scale levels. This situation severely prevents such materials from effective technological applications. The macroscopically aligned mesostructured silica are available by application of strong magnetic fields,[8] reactant flows[9] and capillary flow with an elastic micromold for microcontact printing in electric fields.[10] For thin films, spincasting method[11] or nucleation at interfaces[12,13] are applicable. In such cases, a macro-scale orientation of mesochannels can be attained by deposition on a rubbed surface[14] or a Langmuir-Blodgett (LB) film[15] of polyimide. These facts strongly suggest that nucleation and anisotropic growth of mesoporous silica at an outermost surface of polymer thin films plays a key role to form such aligned mesoporous materials.

Our research group has so far investigated the photocontrol of liquid crystal,[16,17] dye[18] and polymer[19]

alignment on ultrathin films of photoresponsive polymers. Photoirradiation of photochromic Az-containing polymer films with LPL provides the Az films with optical anisotropy due to photoaligned Az chromophores. The anisotropically orientated organic chromophores possess ability to control liquid crystalline materials through van der Waals interaction.
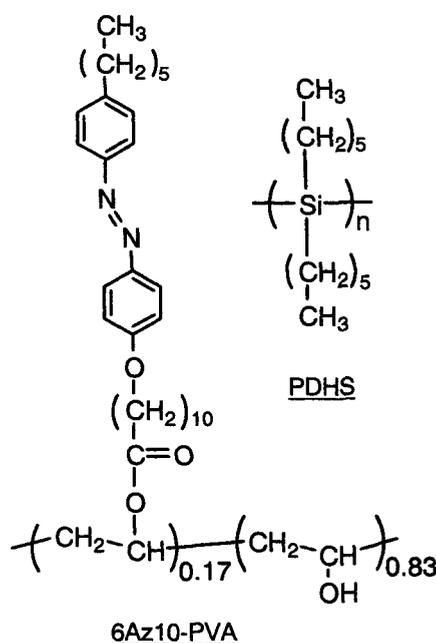
Fig. 1 The chemical structures of the materials in this work.

The research background as mentioned motivated us to investigate photocontrol of mesostructured silica on the photoresponsive polymers. It is anticipated that also a lyotropic liquid crystalline precursor of templating organic surfactants would be aligned at anisotropic polymer interfaces induced by LPL exposure when the sol-gel polymerization of silica proceeds. We report herein the successful photocontrol of mesostructured surfactant/silica hybrids on optically aligned polymer thin films.

2. EXPERIMENTAL

The chemical structures of the materials used in this work are shown in Fig. 1. 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 (1.0 x 10^{-3} mol dm^{-3}) which was pre-irradiated with UV light (365 nm) for 5 min. This monolayer was transferred onto a quartz substrate at a constant pressure, which provides a target molecular area, by the standard vertical dipping method.

The 6Az10-PVA monolayer was then irradiated with non-polarized 365 nm light (0.4 J cm^{-2}) to enrich the cis-Az content and successively with linearly polarized 436 nm light (4.0 J cm^{-2}).[19] 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-44 / V-42 for 436 nm illumination). Films of poly(di-*n*-hexylsilane) (PDHS) (Mw = 4.5 x 10^4) were prepared by spincasting from a hexane solution on the surface of the 6Az10-PVA monolayer. The spincast film of PDHS on the 6Az10-PVA monolayer was first cooled at 0 °C for 60 min, followed by annealing at 100 °C for 10 min, and then cooled again.
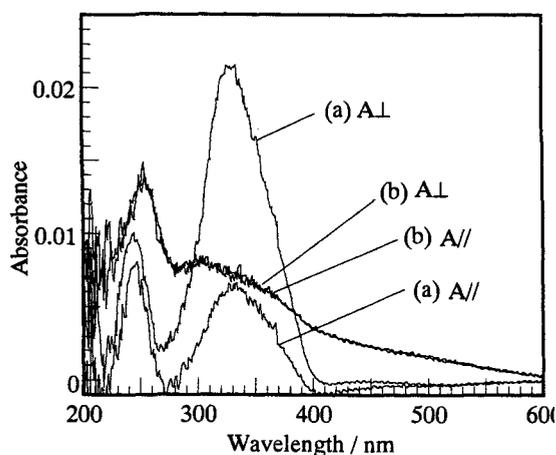
Tetraethoxysilane (TEOS) was mixed with an acidic cationic surfactant hexadecyltrimethylammonium chloride (CTACl) solution, and the mixture was stirred for 2 min at room temperature and transferred into a polypropylene bottle.[12] The molar ratio was TEOS : CTACl : H$_2$O : HCl / 0.10 : 0.11 : 100 : 7.0. The substrate described above was held horizontally in the mixture with the 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. The mesostructured silica films were washed with pure water.

UV-visible absorption spectra were taken on a JASCO MAC-1 spectrophotometer and a Hewlett Packard diode array spectrophotometer. Microscope observation of the morphology of the mesostructured silica film was carried out by using an Olympus BX-60 optical microscope.

3. RESULT AND DISCUSSION

Figure 2(a) shows the polarized UV-Visible absorption spectra of the 6Az10-PVA monolayer irradiated with UV light and LPL. Use of LPL leads to an anisotropic alignment. When liquid crystalline polymer films or LB films possessing a photo-isomerizable unit, most typically Az, are exposed to LPL, the excited molecule undergoes reorientation to a non-excitable direction, namely to the orthogonal direction. This effect is called the photoinduced optical anisotropy or Weigert effect.[20,21]

Here, the photoinduced dichroism of the Az side chains was monitored by dichroic ratio (DR). DR values estimated by polarized absorption spectra are defined as the following equation: $DR=(A_{\perp}-A_{//})/(A_{\perp}+A_{//})$,

Fig. 2 Polarized UV-Visible absorption spectral changes of 6Az10-PVA monolayer before (a) and after (b) immersion in a HCl solution.
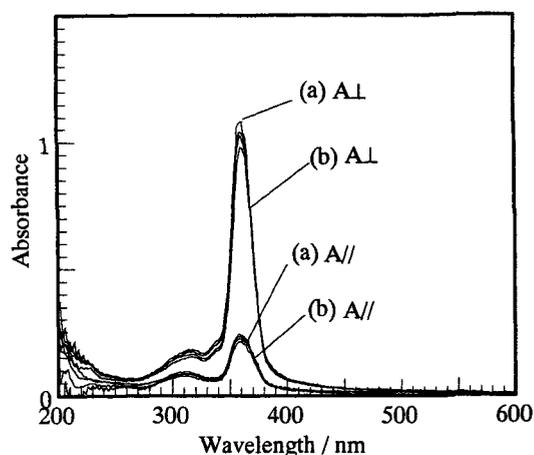
Fig. 3 Polarized UV-Visible absorption spectral changes of PDHS film on 6Az10-PVA monolayer before (a) and after (b) immersion in a HCl solution.
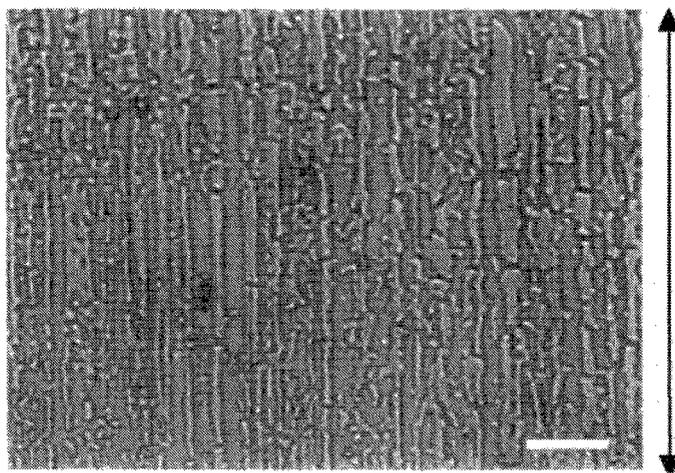
Fig. 4   The optical microscopic image of the deposited surfactant
/silica hybrid on the photoaligned PDHS film.   Scale bar = 10 μm.
Arrow shows the polarization direction of actinic light.

where $A_\perp$ and $A_{//}$ denote absorbance at λ_{max} perpendicular to and in parallel with the electric vector of the polarized light, respectively.   DR of 6Az10-PVA monolayer irradiated with UV light and LPL was 0.53. Irradiation of LPL provides a 6Az10-PVA monolayer aligning perpendicular to the polarization direction caused by the photoinduced optical anisotropy effect.

The optically aligned Az-containing monolayer or thin films in such a way can 'command' orientation of contacting soft matters such as liquid crystals,[16,17] dye aggregates[18] and polymer chains.[19]   The above photo-orienting processes are so far applicable only for soft matters and not for stiff inorganic substances.   Here, we attempted that the surfactant templated silicate is an intriguing candidate for photo-orientation because such hybrid mesophases are synthesized via sol-gel polymerization starting form a fluid lyotropic liquid crystalline precursor.

DR of a 6Az10-PVA monolayer became completely zero after immersion into a HCl aq. solution, which was the condition adopted for the siloxane condensation (Fig. 2(b)).   Conformation of the 6Az10-PVA on the substrate was disordered by immersion into HCl aq. solution.   Attempts of direct deposition of the surfactant templated silica onto the Az monolayer were unsuccessful because the conditions adopted for the siloxane condensation crucially damaged the orientation of Az layer.

To retain the orientation of the monolayer after immersion into HCl aq. solution, a spincast film of PDHS was first prepared on the 6Az10-PVA monolayer. After sufficient crystallization of the PDHS film at 0 °C, this film was optically highly anisotropic.[19]   Figure 3 shows the polarized UV-visible absorption spectra of the PDHS film.   These spectra were revealed that the Si

main chain in the crystalline phase is aligned perpendicular to the polarization plane of the irradiating light.   The orientational order parameter, S [=($A_\perp$-$A_{//}$)/($A_\perp$+2$A_{//}$)], where $A_\perp$ and $A_{//}$ denote absorbance at the spectral peak (368 nm) observed in the perpendicular and parallel direction with respect to the polarization direction of the initial actinic light, was 0.55.   The electric transition moment of the polysilane backbone is along the Si backbone orientation.   Thus, the spectra show that the Si backbone is aligned perpendicular to the polarization plane of the light, which is in accord with the direction of the photoaligned Az layer.   S of the PDHS film on the Az monolayer was kept unchanged into a HCl aq. solution at room temperature for a week.   From these results, the surface of the photoaligned PDHS films was desirable to synthesize mesostructured surfactant/silica hybrids.   Consequently, the orientation of the Si main chain of the PDHS film exhibited excellent chemical stability under such acidic conditions and could be regarded as the orientation fixer of the Az monolayer.

Figure 4 shows the optical microscopic image of the deposited surfactant/silica hybrid on the photoaligned PDHS film.   Uniaxially aligned elongated particles with widths of a micrometer range were observed. Orientation of each particle was aligned parallel to each other and the direction of the long axis of the particles was in perpendicular to the Si backbone direction.   This indicates that the orientation of elongated particles are aligned parallel to the polarization direction of pre-irradiated polarized actinic light.   Non-oriented surface yielded round and spherical surfactant/silica particles. Thus, the elongation of the particle strongly suggests the alignment of the mesochannels.   The structural characterization of this film is now in progress.

4. CONCLUSION

An attempt to align meso-channeled silica in the anisotropic photochemical process was undertaken. This paper presented some results obtained at a preliminary stage. The direct orientational transfer from the Az monolayer to the meso-structured surfactant/silica hybrid was found to be unsuccessful. The successful alignment of the surfactant/silica hybrid required a first orientational fixation using a polysilane film. The elongated silica particles were aligned parallel to the direction of the actinic polarized light. The optimization of the preparative conditions and characterizations by X-ray diffraction of the photoaligned silica hybrids are now underway.

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