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Change in Molecular Orientation with Condensation of 4,4′-Bis(trihydroxysilyl)biphenyl Crystals

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Molecular orientation in 4,4′-bis(trihydroxysilyl)biphenyl plate-like square crystals (BPSi) and orientation change with heating-induced condensation were investigated using polarization optical microscopy. The biphenylylene groups in BPSi were arranged along a diagonal of the square plane with a tilt angle of 21° from the planar normal. This arrangement was maintained up to 200 °C for several minutes, but heating at 250 °C promoted a condensation reaction which formed siloxane bonds, causing changes in molecular orientation to a tilt angle of 0°, and altering the shape of BPSi crystals from square to rhombic. The molecular arrangement and its change after condensation were qualitatively confirmed by molecular-mechanics simulation. The absorption and fluorescence bands of the biphenylylene groups were significantly red-shifted by the condensation due to the change in molecular arrangement, which resulted from a notable decrease in biphenylylene–biphenylylene separation.

Organic–silica hybrid materials derived from polycondensation of bridged organosilane precursors $[(R'O)_3Si–R–Si(OR')_3]$ have attracted much attention because various functionalities can be introduced by proper selection of bridging organic groups (–R–).[1,2] Moreover, bridged organosilane precursors with specific R groups exhibiting strong interaction have a unique ability of self-organization, forming ordered organosilica materials.[3,4] For example, Moreau et al. reported self-organized hybrid organosilicas with helical morphology[5] and a long-range-ordered lamellar structure[6,7] from strongly interacting ureid group-bridged organosilane precursors. As an alternate route, Boury et al. proposed solid-state hydrolysis/polycondensation of organo-bis-trichlorosilane[8] and organo-bis-trialkoxysilane[9] molecular crystals to obtain organosilica solids with highly ordered structure. Cerveau et al. also reported mild thermal polycondensation of organo-bis-trihydroxysilane crystals to form organosilica solids with a long-range-ordered lamellar structure.[10] Self-organization of bridged organosilanes containing simple aromatic groups (e.g., phenylene and biphenylylene) has also been observed in a framework of periodic mesoporous[11,12] and non-porous organosilicas.[13] These highly-organized organosilica materials are expected to exhibit unique optical and electrical properties due to the specific arrangement and/or interaction of organic groups in the solids.

Recently, Pang et al. reported syntheses of plate-like biphenylylene–silica particles with a long-range-ordered lamellar structure and well-defined single crystal-like morphology by thermal polycondensation of 4,4′-bis(trihydroxysilyl)biphenyl crystals (BPSi).[14] A well-defined plate-like morphology is greatly advantageous in application to electrical and optical devices. Although X-ray diffraction studies revealed that BPSi and condensed BPSi had monoclinic[14,15] and lamellar[14] symmetries, respectively, the detailed arrangement and orientation of the biphenylylene groups in these plate-like particles is not yet well-understood. Here, we report the molecular arrangement and orientation of the biphenylylene groups in BPSi and condensed BPSi using polarization optical microscopy. The biphenylylene groups in BPSi were arranged along a diagonal of the square plate with a tilt angle of 21°. Solid-state condensation of BPSi caused heating-induced changes in the molecular orientation to a tilt angle of 0°, and altered the shape of the particles from square to rhombic.

Results and Discussion

Figure 1 shows SEM images of BPSi exhibiting a uniform square plate-like morphology with side lengths (*X* or *X*′ axis in Figure 1b) of 7–11 μm and thicknesses (*Y* axis in Figure 1b) of 1–2 μm.[16] The XRD pattern from BPSi indicated a monoclinic crystal structure (Figure S1a). The intense diffraction at

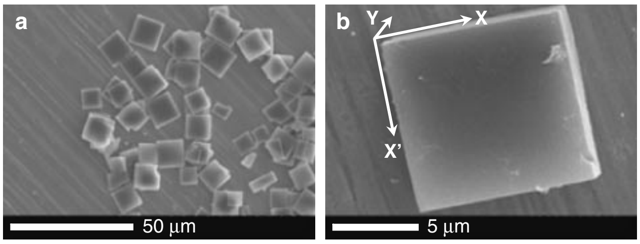

Figure 1. Scanning electron microscopy images of 4,4′-bis(trihydroxysilyl)biphenyl crystals (BPSi); a: low-magnification image, b: high-magnification image.

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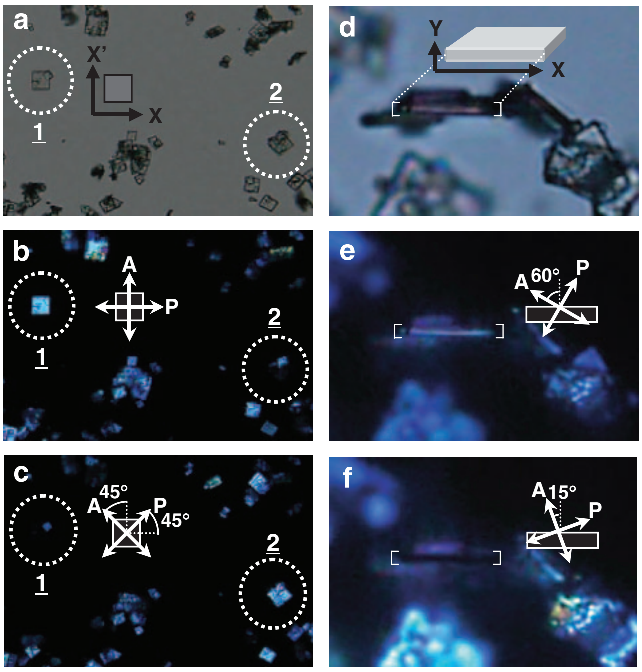
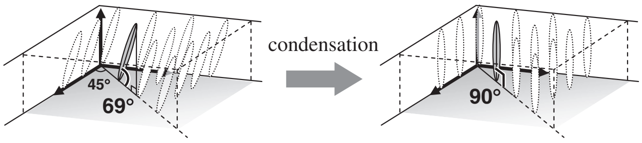


Figure 2. Non-polarized (a and d) and polarized (b, c, e, and f) optical micrographs of BPSi. Observations were carried out to the *X*–*X*′ (a, b, and c) and *X*–*Y* (d, e, and f) planes of BPSi. Black arrows in the non-polarized micrographs indicate directions of the crystal axes. White arrows in the cross-polarized micrographs indicate crossed polarization directions (P: polarizer, A: analyzer).

$2\theta = 6.31°$ corresponds to a lamellar spacing of 1.40 nm where the hydrolyzed precursor molecules are arranged in a head-to-tail manner to form a lamellar structure consisting of alternating hydrophilic trihydroxysilyl and hydrophobic biphenylylene layers. The ^{29}Si MAS NMR showed only T^0 species (T^n: R–$Si(OH)_{3-n}(OSi)_n$), indicating no condensation of hydrolyzed precursor molecules (Figure S2). These results are in agreement with those of the previous report.[14] In addition, the selected area electron diffraction of BPSi confirmed that lamellar ordering existed along the *Y* axis.

Figure 2 shows non-polarized (a and d) and polarized (b, c, e, and f) optical micrographs of BPSi. The crystals exhibited uniform birefringent behavior over their entirety. In the left micrographs (Figures 2a–2c), we marked two crystals (1 and 2) showing the *X*–*X*′ planes clearly with different rotation angles in the *X*–*X*′ plane (Figure 2a). The optical images were brightest when the polarization direction was parallel to the *X* or *X*′ axis (crystal 1 in Figure 2b and crystal 2 in Figure 2c), and darkest when the polarization direction was 45° from the *X* or *X*′ axis (crystal 2 in Figure 2b and crystal 1 in Figure 2c). This indicates that an optical axis exists in the diagonal direction of the *X*–*X*′ plane of BPSi, and suggests that the biphenylylene groups in BPSi are tilted in this direction within the *X*–*X*′ plane. On the other hand, the *X*–*Y* plane showed the brightest and darkest images when the polarization directions were 60 and 15° from the *Y* axis, respectively (Figures 2e and 2f). This indicates that an optical axis exists at a 15° angle from the *Y* axis, suggesting that the biphenylylene groups of BPSi are tilted in this direction in the *X*–*Y* plane. The tilt angle of 15° in the *X*–*Y* plane corresponds to that of 21° for the diagonal direction in the *X*–*X*′ plane. According to these observations, we conclude that the biphenylylene bis-silanetriol molecules in BPSi are arranged along the diagonal direction in the *X*–*X*′ plane with a tilt angle of 21° from the *Y* axis, as illustrated in Figure 3a.



(a) (b)

Figure 3. Experimentally presumed molecular arrangements of the biphenylylene groups in BPSi (a) and heat-treated BPSi (b).

The BPSi crystals were heated at 200 °C for 8 h to promote a condensation reaction of the bis-silanetriols. A formation of siloxane bonds from the silanol groups was confirmed by ^{29}Si MAS NMR of heat-treated BPSi due to the appearance of T^2 and T^3 signals and the disappearance of the T^0 signal (Figure S2b). The XRD pattern of heat-treated BPSi showed only two peaks at $2\theta = 7.01$ and 14.1°, due to a lamellar structure with an interlayer spacing of 1.26 nm, and no peaks at wider angles (Figure S1b). This indicates that the condensation reaction brings about a large shrinkage of the interlayer spacing (from 1.40 to 1.26 nm) and a perturbation of the molecular periodicity within the lamellar structure. Polarization optical microscopy showed only dark images in the *X*–*X*′ plane for all polarization directions, indicating no optical anisotropy in the *X*–*X*′ plane of heat-treated BPSi (Figures 4a–4c). The optical images in the *X*–*Y* plane were darkest and brightest when the polarization directions were 0° (or 90°) and 45° from the *Y* axis, respectively, indicating that an optical axis exists parallel to the *X* and *Y* directions in the *X*–*Y* plane (Figures 4d–4f). These results strongly suggest that the molecular axes of the biphenylylene groups were directed parallel to the *Y* axis of BPSi, as illustrated in Figure 3b.

The change of molecular arrangement in BPSi upon heating was also observed by in situ polarization optical microscopy at elevated temperature (Figures 5a–5d). No change was observed at 100 or 200 °C over several minutes (Figures 5a and 5b), but the central area of the BPSi sample became dark immediately upon reaching 250 °C (Figure 5c). The dark area spread outward and occupied of the entire BPSi area after 20 min (Figure 5d) when the temperature was maintained at 250 °C, corresponding to disappearance of the optical anisotropy of heat-treated BPSi (Figure 4). Interestingly, the shape of BPSi also changed, from square to rhombic, with the change in molecular arrangement, as clearly confirmed by comparison of the non-polarized optical microscopic images of BPSi heated at 100 and 250 °C (20 min) (Figures 5e and 5f). The shrinking diagonal was coincident with the tilt direction of the biphenylylene groups in BPSi, as confirmed by polarization optical microscopy with a 530 nm retardation plate placed perpendicular and parallel to the short diagonal direction of heat-treated BPSi (Figure S3). The anisotropic shrinkage of BPSi upon heating is attributed to the change in tilt angle of the biphenylylene groups in BPSi.

Molecular-mechanics simulations of the molecular arrangements in uncondensed and condensed BPSi were carried out in order to confirm the change in tilt angle of the biphenylylene groups after condensation. The simulation showed that the tilt angles of the biphenylylene groups were 16.6 and 7.6° for uncondensed and condensed BPSi, respectively (Figure 6), which qualitatively explain the experimental results, although the calculated change in the tilt angle (from 16.6 to 7.6°) was smaller than the measured change (from 21 to 0°). The interlayer spacing of the simulated models, 1.40 and 1.19 nm for uncondensed and condensed BPSi, respectively (Figure 6), were very close to the experimental results.

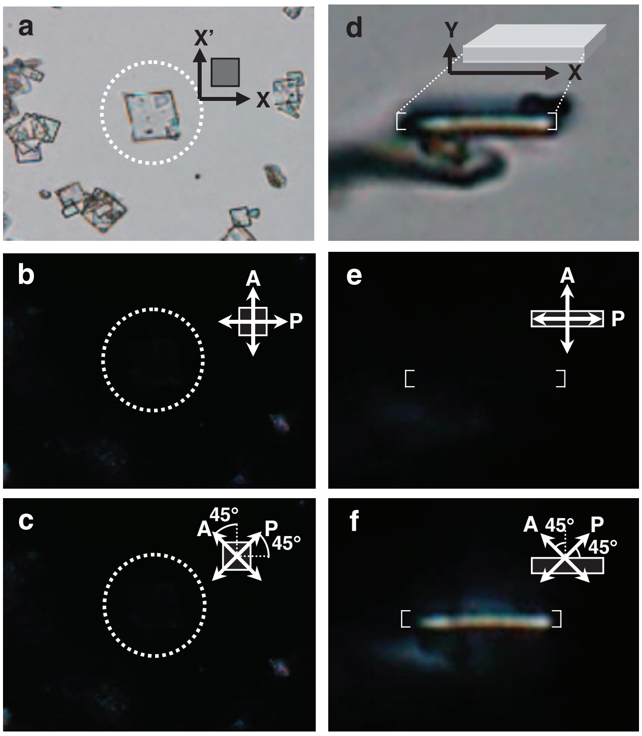


Figure 4. Non-polarized (a and d) and polarized (b, c, e, and f) optical micrographs of heat-treated BPSi. Observations of the *X*–*X*′ (a, b, and c) and *X*–*Y* (d, e, and f) planes of BPSi were carried out. Black arrows in the non-polarized micrographs indicate the direction of crystal axes. White arrows in the cross-polarized micrographs indicate crossed polarization directions (P: polarizer, A: analyzer).

Figure 7 shows fluorescence emission spectra of BPSi and heat-treated BPSi excited at 280 nm. The emission from the biphenylylene groups in BPSi (347 nm) was red-shifted to 380 nm in heat-treated BPSi due to an enhanced interaction between closer-packed biphenylylene groups, consistent with the change in molecular arrangement resulting from the condensation of BPSi. The absorption spectrum of heat-treated BPSi was also red-shifted (Figure S4). These results suggest that the optical properties of BPSi can be tuned by controlling the condensation reaction.

Conclusion

The molecular orientation in BPSi and its change after heat-induced condensation were investigated by polarization optical microscopy. The biphenylylene groups in BPSi were arranged along the diagonal of the *X*–*X*′ plane with a tilt angle of 21° from the *Y* axis. Condensation of BPSi with heating caused a

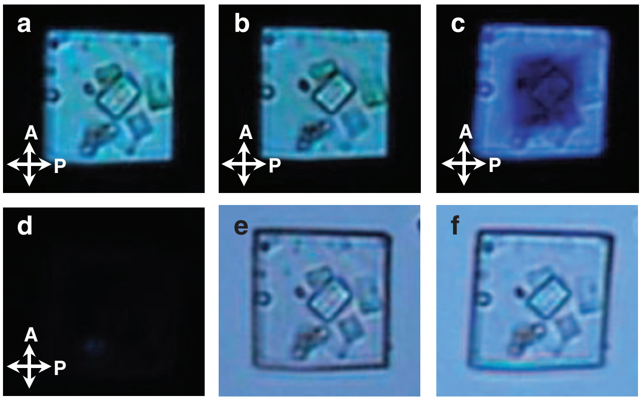


Figure 5. Polarized (a, b, c, and d) and non-polarized (e and f) optical micrographs of BPSi at elevated temperatures; a: 100 °C, b: 200 °C, c: 250 °C, d: after 20 min at 250 °C, e: 100 °C, and f: 250 °C (20 min). Arrows in the figures indicate crossed polarization directions (P: polarizer, A: analyzer).

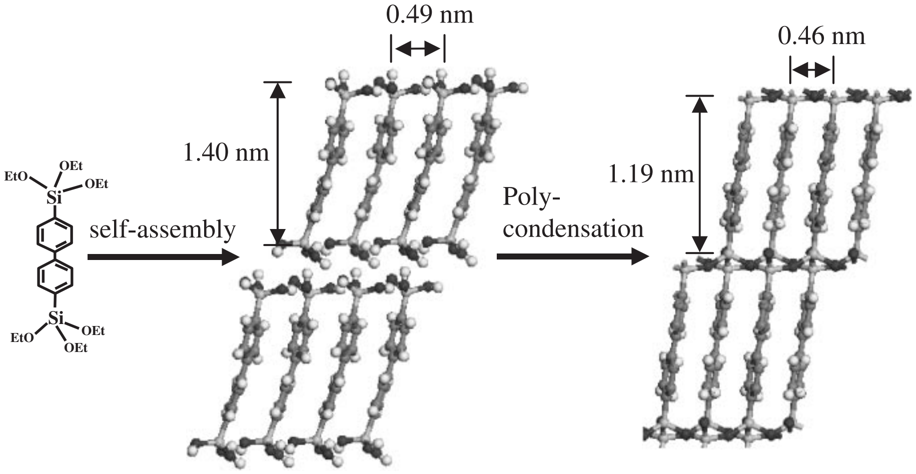


Figure 6. Simulated models of the molecular arrangements in BPSi and heat-treated BPSi.

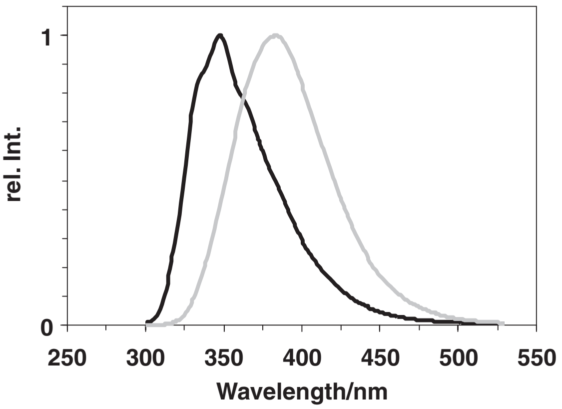


Figure 7. Fluorescence emission spectra of BPSi (black) and heat-treated BPSi (gray) excited at 280 nm.

change in molecular orientation to a tilt angle of 0° and changed the crystal shape from square to rhombic. The molecular arrangement and its change after condensation were qualitatively confirmed by molecular-mechanics simulation. The absorption and fluorescence emission spectra were red-shifted by condensation due to enhanced interaction between more closely packed biphenylylene groups, consistent with the observed change in molecular arrangement.

Experimental

Materials. 4,4′-Bis(triethoxysilyl)biphenyl (BTEBP) was purchased from Nard Research Institute Co., Ltd. The other chemicals were purchased from Aldrich and Wako Chemicals. All chemicals were used without further purification.

Sample Preparation. The 4,4′-bis(trihydroxysilyl)biphenyl crystals (BPSi) were prepared according to a previously reported method.[14] BTEBP (0.55 mL) was added dropwise to a mixed solution containing Pluronic P123 (1 g), distilled water (36 g), and 37 wt % HCl (1 mL) at 0 °C. Then, the reaction mixture was stirred at 30 °C for 3 days. A formed white precipitate, BPSi, was recovered by filtration, washed with water, and dried in vacuo.

Characterization. Morphology was observed by scanning electron microscopy (SEM: Hitachi S-3600N). Prior to analysis, samples on copper plates were coated with Au by ion coater (Eiko Engineering, IB-5). Periodicity was evaluated by powder X-ray diffraction (XRD: Rigaku Rint-TTR) using Cu Kα radiation ($\lambda = 1.5418$ Å) with 2θ values ranging from 1 to 40°. Bonding states were characterized by ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR: Bruker AVANCE 400) with a MAS spinning rate of 5 kHz. The molecular orientation in the crystal was estimated by polarization optical microscope (Olympus BX51) under cross-Nicol condition. Thermo-optical analysis was carried out by polarization optical microscopy with a hot stage (Mettler Toledo FP 82HT) connected to a central processor (Mettler Toledo FP 90). The micrographs were recorded by a digital camera system (Olympus DP20). Ultraviolet–visible light (UV–vis) absorption spectra were obtained using a double-beam spectrophotometer (JASCO V-670). Fluorescence emission spectra were measured by spectrofluorometer (JASCO FP-6500ST).

Structural Simulation. Simulation of molecular arrangements in BPSi was performed using integrated simulation software Materials Studio (Accelrys). The molecular arrangements were optimized by an energy minimization method under the COMPASS force field with reference to the reported unit cell parameters of BPSi.[14]

Supporting Information

X-ray diffraction patterns, ^{29}Si magic-angle spinning NMR spectra, polarized optical microscopic images taken with a 530 nm retardation plate, and UV–vis absorption spectra of BPSi and heat-treated BPSi. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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16 The uniform plate-like morphology was not obtained for synthesis without the surfactant.[13] The surfactant initially forms an emulsion with the hydrophobic organosilane precursor, which may slow its hydrolysis reaction and limit new nucleus formation. Furthermore, the surfactant is considered to play an important role for the preferred crystal growth in the *X*–*Y* plane (Figure 1) because the surfactant can interact with silanol groups in the *X*–*X*′ plane and suppress the crystal growth in this plane.