

Supporting Information

Self-Healing Lamellar Silsesquioxane Thin Films

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Additional experimental details

Materials

1,2-Bis(triethoxysilyl)ethane (BTSE, >96.0%) was purchased from Sigma-Aldrich; tetraethoxysilane (TEOS, 99%) was purchased from Kishida Chemical Co., Ltd; 1,2-bis(triethoxysilyl)ethylene (BTSV) and 1,4-bis(triethoxysilyl)benzene (BTSEB) were purchased from Gelest Inc.; didodecyldimethylammonium bromide (DDAB, >98.0%), allyltriethoxysilane (>96.0%), vinyltriethoxysilane (>98.0%), 2,2'-azobis(isobutyronitrile) (AIBN, >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd; 1,2-ethanedithiol (>99.0%), 1,6-hexanedithiol (>96.0%), 1,10-decanedithiol (>96.0%), toluene (super dehydrated, 99.5%), HCl aq. (0.1 and 6 N) were purchased from Wako Pure Chemical Industries, Ltd; ethanol (>99.5%) was purchased from Junsei Chemical Co., Ltd. These chemicals were used without further purification. Si (100) substrates were purchased from Silicon Technology Co., Ltd. Silicone rubber sheet (2 mm thick) was purchased from AS ONE Corp. and used as PDMS substrates.

Synthesis of organo-bridged alkoxy-silanes with long organic chains.

BTSC₁₂ [(EtO)₃Si(CH₂)₃S(CH₂)₆S(CH₂)₃Si(OEt)₃] was synthesized by the thiol-ene reaction of allyltriethoxysilane (0.0132 mol) and 1,6-hexanedithiol (0.006 mol) in toluene (24 mL) in the presence of AIBN (0.0003 mol). After stirring the mixture at 80 °C for 2 d in a nitrogen atmosphere, the solvent was removed under vacuum. Finally, BTSC₁₂ was isolated by gel permeation chromatography (GPC) using chloroform as an eluent (colorless liquid, yield: 54% based on Si). ¹H NMR (δ, 500 MHz, CDCl₃): 0.73–76 (t, 4H, SCH₂CH₂CH₂Si), 1.18–1.24 (m, 18H, SiOCH₂CH₃), 1.40 (brs, 4H, SCH₂CH₂CH₂CH₂CH₂CH₂S), 1.58 (brs, 4H, SCH₂CH₂CH₂CH₂CH₂CH₂S), 1.67–1.73 (m, 4H, SCH₂CH₂CH₂Si), 2.45–2.55 (m, 8H, SiCH₂CH₂CH₂SCH₂CH₂CH₂CH₂CH₂CH₂CH₂SCH₂CH₂CH₂Si), 3.79–3.84 (m, 12H, SiOCH₂CH₃). ¹³C NMR (δ, 500 MHz, CDCl₃): 9.95 (SCH₂CH₂CH₂Si), 18.33 (SiOCH₂CH₃), 23.29 (SCH₂CH₂CH₂Si), 28.60 (SCH₂CH₂CH₂CH₂CH₂CH₂S), 29.67 (SCH₂CH₂CH₂CH₂CH₂CH₂S), 31.85 (SCH₂C₄H₈CH₂S), 35.22 (SCH₂CH₂CH₂Si), 58.50 (SiOCH₂CH₃). ²⁹Si NMR (δ, 500 MHz, CDCl₃): –45.65. ESI-MS: *m/z* 581.24 [M + Na]⁺.

BTSC₁₀ [(EtO)₃Si(CH₂)₂S(CH₂)₆S(CH₂)₂Si(OEt)₃] was synthesized by the thiol-ene reaction of vinyltriethoxysilane (0.0132 mol) and 1,6-hexanedithiol (0.006 mol) in toluene (24 mL) in the presence of AIBN (0.0003 mol). After stirring the mixture at 80 °C for 2 d in a nitrogen atmosphere, the solvent was removed under vacuum. Finally, BTSC₁₀ was isolated by GPC using chloroform as an eluent (colorless liquid, yield: 58% based on Si). ¹H NMR (δ, 500 MHz, CDCl₃): 0.93–1.00 (t, 4H, SCH₂CH₂Si), 1.18–1.24 (m, 18H, SiOCH₂CH₃), 1.39 (brs, 4H, SCH₂CH₂CH₂CH₂CH₂CH₂S), 1.57 (brs, 4H, SCH₂CH₂CH₂CH₂CH₂CH₂S), 2.47–2.54 (m, 4H, SCH₂CH₂Si), 2.57–2.64 (m, 4H, SCH₂CH₂CH₂CH₂CH₂CH₂S), 3.77–3.85 (m, 12H, SiOCH₂CH₃). ¹³C NMR (δ, 500 MHz, CDCl₃): 11.87 (SCH₂CH₂Si), 18.31 (SiOCH₂CH₃), 26.30 (SCH₂CH₂Si), 28.62 (SCH₂CH₂CH₂CH₂CH₂CH₂S), 29.64 (SCH₂CH₂CH₂CH₂CH₂CH₂S), 31.79 (SCH₂C₄H₈CH₂S), 58.51 (SiOCH₂CH₃). ²⁹Si NMR (δ, 500 MHz, CDCl₃): –48.07. ESI-MS: *m/z* 553.21 [M + Na]⁺.

BTSC₈ [(EtO)₃Si(CH₂)₃S(CH₂)₂S(CH₂)₃Si(OEt)₃] was synthesized by the thiol-ene reaction of allyltriethoxysilane (0.0132 mol) and 1,2-ethanedithiol (0.006 mol) in toluene (24 mL) in the presence of AIBN (0.0003 mol). After stirring the mixture at 80 °C for 2 d in a nitrogen atmosphere, the solvent was removed under vacuum. Finally, BTSC₈ was isolated by GPC using chloroform as an eluent (colorless liquid, yield: 57% based on Si). ¹H NMR (δ, 500 MHz, CDCl₃): 0.72–0.76 (t, SCH₂CH₂CH₂Si), 1.19–1.26 (m, 18H, SiOCH₂CH₃), 1.68–1.74 (m, 4H, SCH₂CH₂CH₂Si), 2.56–2.59 (t, 4H, SCH₂CH₂CH₂Si), 2.71 (s, SCH₂CH₂S), 3.80–3.84 (q, 12H, SiOCH₂CH₃). ¹³C NMR (δ, 500 MHz, CDCl₃): 9.90 (SCH₂CH₂CH₂Si), 18.32 (SiOCH₂CH₃), 23.30 (SCH₂CH₂CH₂Si), 32.09 (SCH₂CH₂S), 35.20 (SCH₂CH₂CH₂Si), 58.42 (SiOCH₂CH₃). ²⁹Si NMR (δ, 500 MHz, CDCl₃): –45.84. ESI-MS: *m/z* 525.22 [M + Na]⁺.

Liquid-state NMR analysis

Liquid-state ^1H , ^{13}C and ^{29}Si NMR spectra of BTSC_n were recorded on a JEOL JNM ECZ 500 spectrometer at resonance frequencies of 500.16, 125.77, and 99.37 MHz, respectively, at ambient temperature using 5 mm glass tubes. Tetramethylsilane was used as an internal reference ($\delta = 0$ ppm). Chloroform-*d* was used to obtain lock signals. A small amount of Cr(acac)₃ (acac = acetylacetonate) was used as a relaxation agent for ^{29}Si nuclei. The ^{29}Si NMR spectra were measured with a 45° pulse and recycle delay of 10 s.

Preparation of silica-based lamellar thin films

Silica-based lamellar thin films were prepared from a precursor solution with the molar composition of TEOS:DDAB:EtOH:H₂O:HCl = 2:0.4:30:10:0.4, following our previous report (S. Itoh et al, *ACS Nano*, 2017, **11**, 10289). The precursor solutions after stirring at 60 °C for 24 h or for 72 h were spin-coated on Si substrates or on PDMS substrates.

Additional data

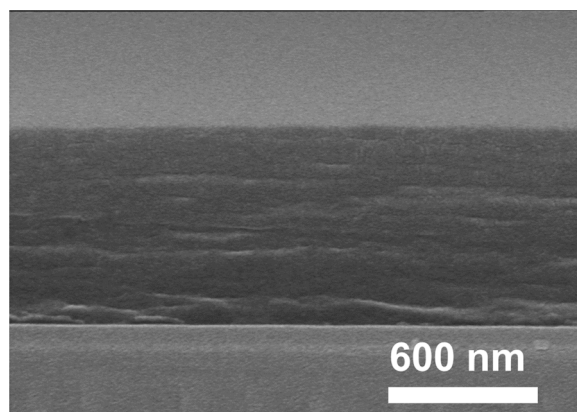


Figure S1 Cross-sectional SEM image of the lamellar thin film prepared using BTSE and DDAB.

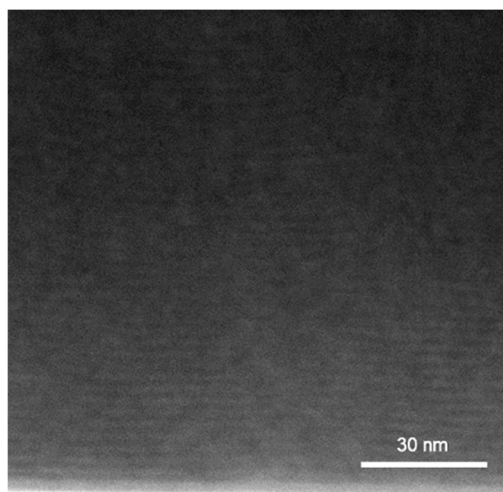


Figure S2 Cross-sectional STEM image of the lamellar thin film prepared using BTSE and DDAB. The region near the substrate surface was observed.

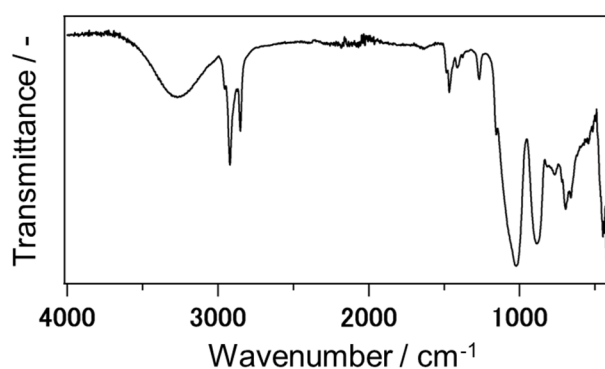


Figure S3 ATR-FTIR spectrum of the lamellar thin film prepared using BTSE and DDAB.

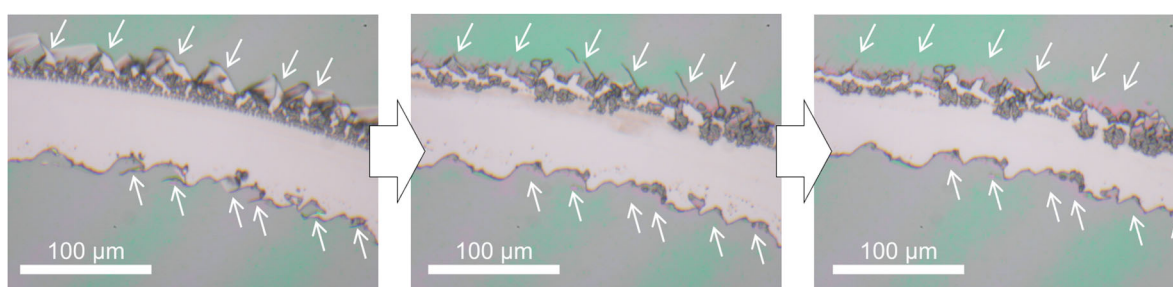


Figure S4 Optical microscopy images showing the changes of the crack appearance for the lamellar thin film prepared using BTSE and DDAB (DDAB/BTSE = 0.4). The film after scratching with a syringe needle was exposed to a humid air ($>90\%$ RH) at room temperature. The white arrows indicate the cracks propagated from the scratch.



Figure S5 SEM image of an indent made on a Si substrate by a Knoop indenter with a load of 49 mN.

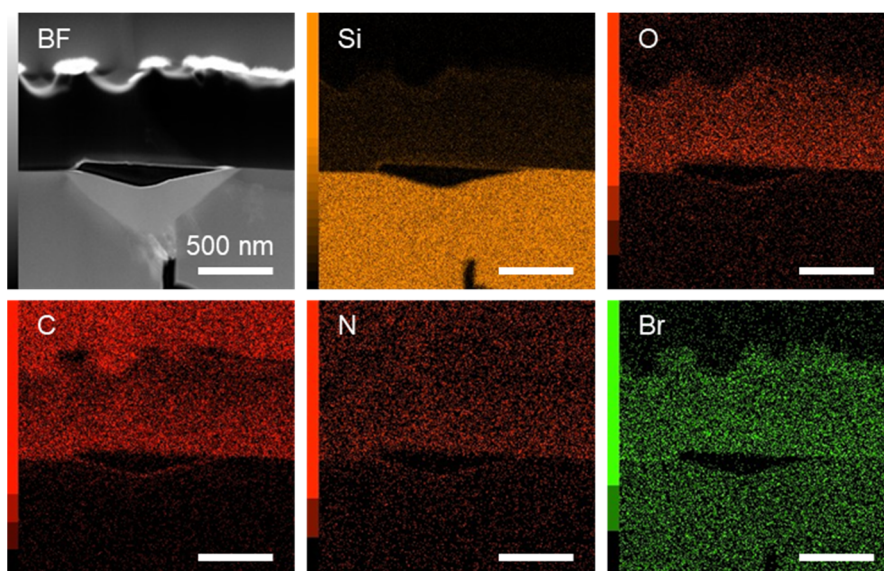


Figure S6 STEM-EDS mapping of the cross-section of the silsesquioxane-based lamellar thin film prepared using BTSE and DDAB (scale bars: 500 nm). The sample is the same as that shown in Figure 3d.

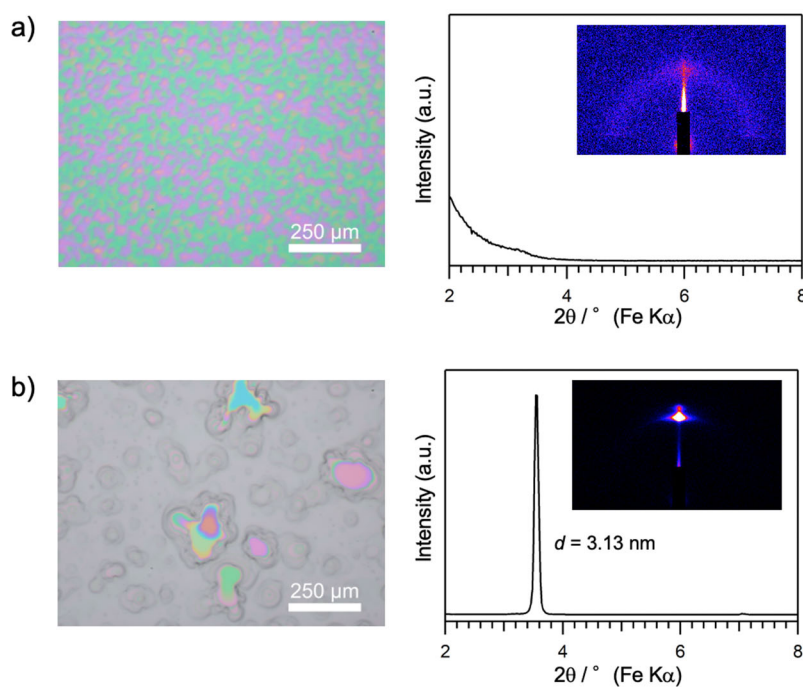


Figure S7 (Left) Optical microscopy images and (right) XRD patterns and GI-SAXS patterns (insets) of the thin films prepared at the molar ratios of DDAB/BTSE = (a) 0.2 and (b) 0.8.

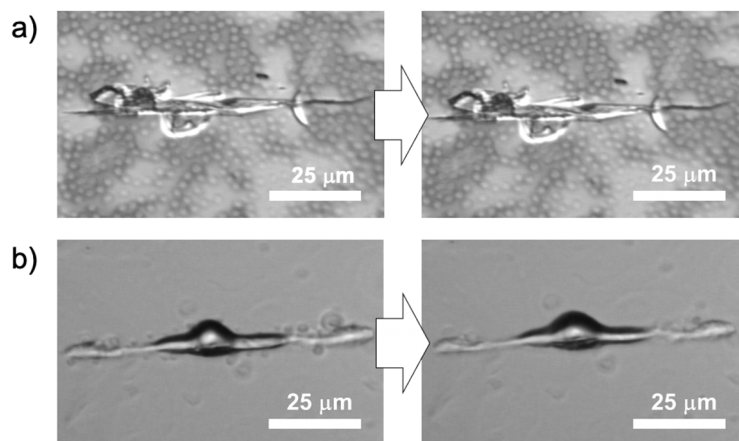


Figure S8 Optical microscopy images of the thin films prepared at the molar ratios of DDAB/BTSE = (a) 0.2 and (b) 0.8: (left) just after pressing a Knoop indenter with a load of 490 mN and (right) after 5 min at 22 $^\circ\text{C}$ and 66% RH.

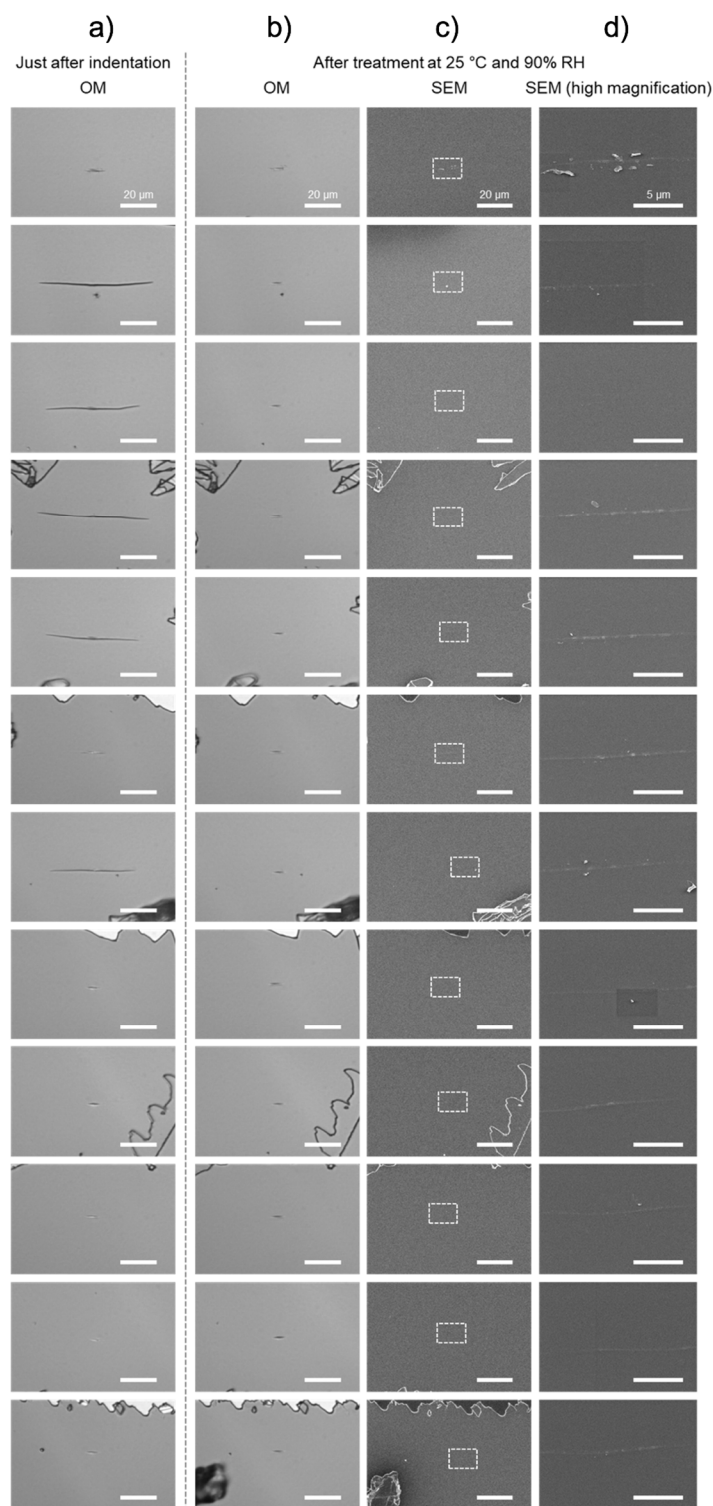


Figure S9 Optical microscopy (OM) images of the silsesquioxane-based lamellar thin film prepared using BTSE and DDAB: (a) just after pressing a Knoop indenter at 22 °C and 57% RH and (b) after subsequent treatment at 25 °C and >90% RH. (c) and (d) show the low and high magnification SEM images of the films after the treatment at 25 °C and >90% RH, respectively. The cracks were made near the large scratch made with a needle so that the same regions could be easily observed by OM and SEM.

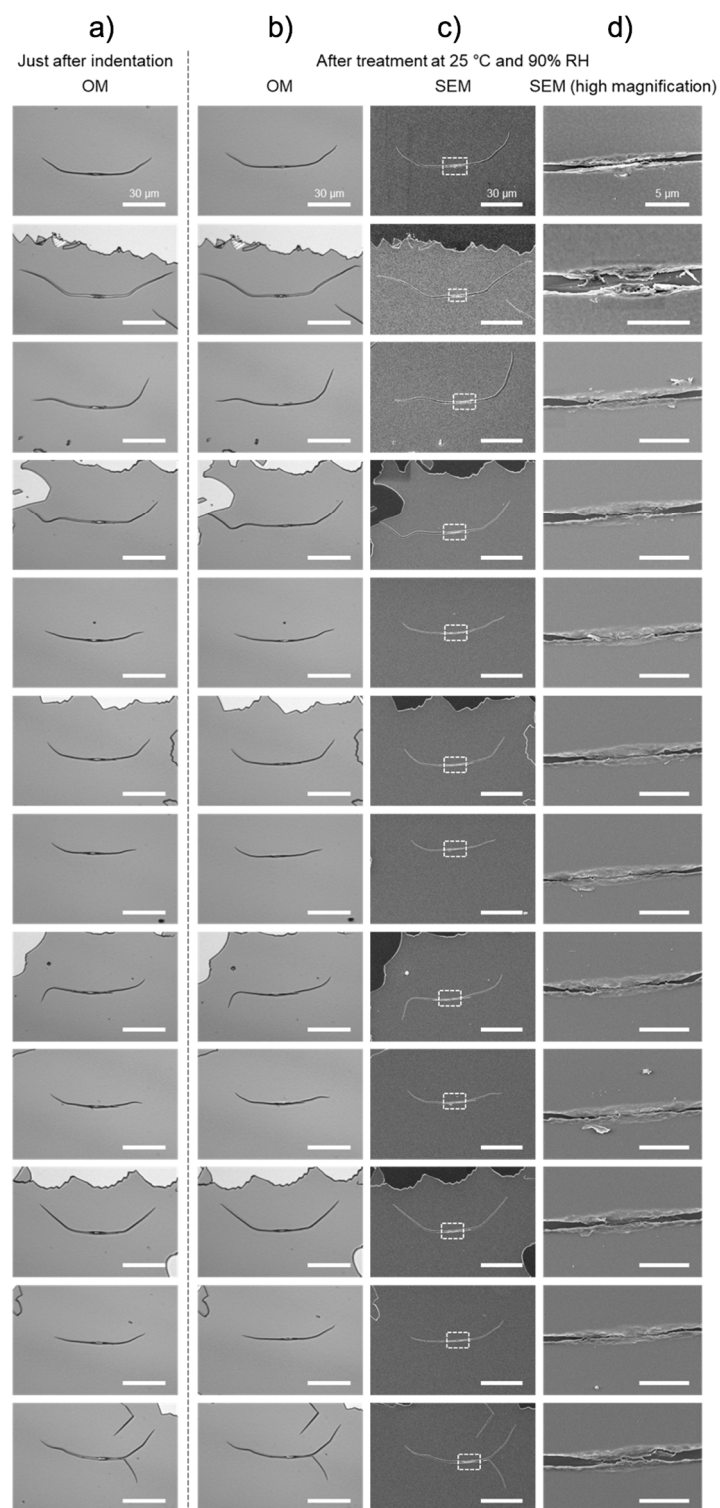


Figure S10 Optical microscopy (OM) images of the silica-based lamellar thin film prepared using TEOS and DDAB: (a) just after pressing a Knoop indenter at 22 °C and 57% RH and (b) after subsequent treatment at 25 °C and >90% RH. (c) and (d) show the low and high magnification SEM images of the films after the treatment at 25 °C and >90% RH, respectively. The cracks were made near the large scratch made with a needle so that the same regions could be easily observed by OM and SEM.

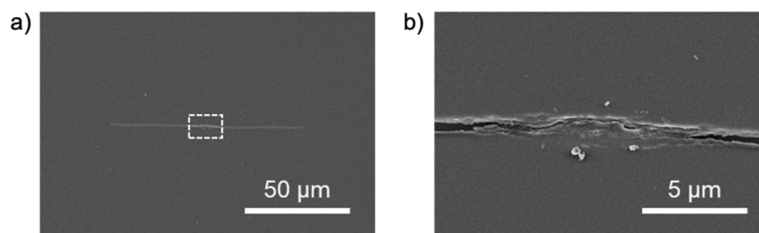


Figure S11 (a) SEM image of the crack formed on a silica-based lamellar film (random orientation) after the treatment at >90% RH (humid air flow). (b) High magnification SEM image of the area indicated with a white dotted square in the image (a).

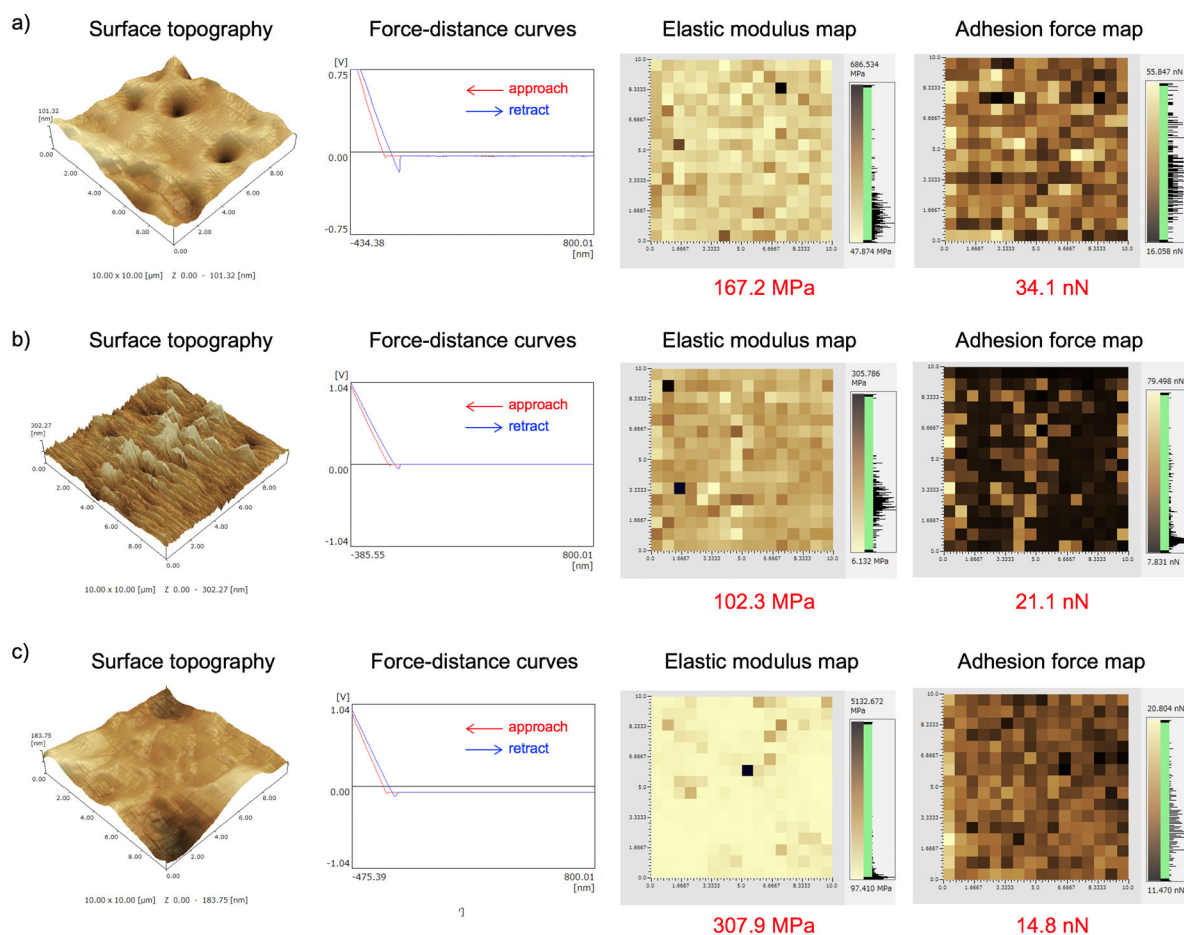


Figure S12 AFM surface topographies, force-distance curves, elastic modulus maps, and adhesion force maps of (a) silica-based lamellar thin film prepared using TEOS and DDAB, (b) silsesquioxane-based lamellar thin film prepared using BTSE and DDAB and (c) silsesquioxane-based lamellar thin film prepared using BTSE, BTSC₁₄, and DDAB (BTSC₁₄/BTSE = 0.14).

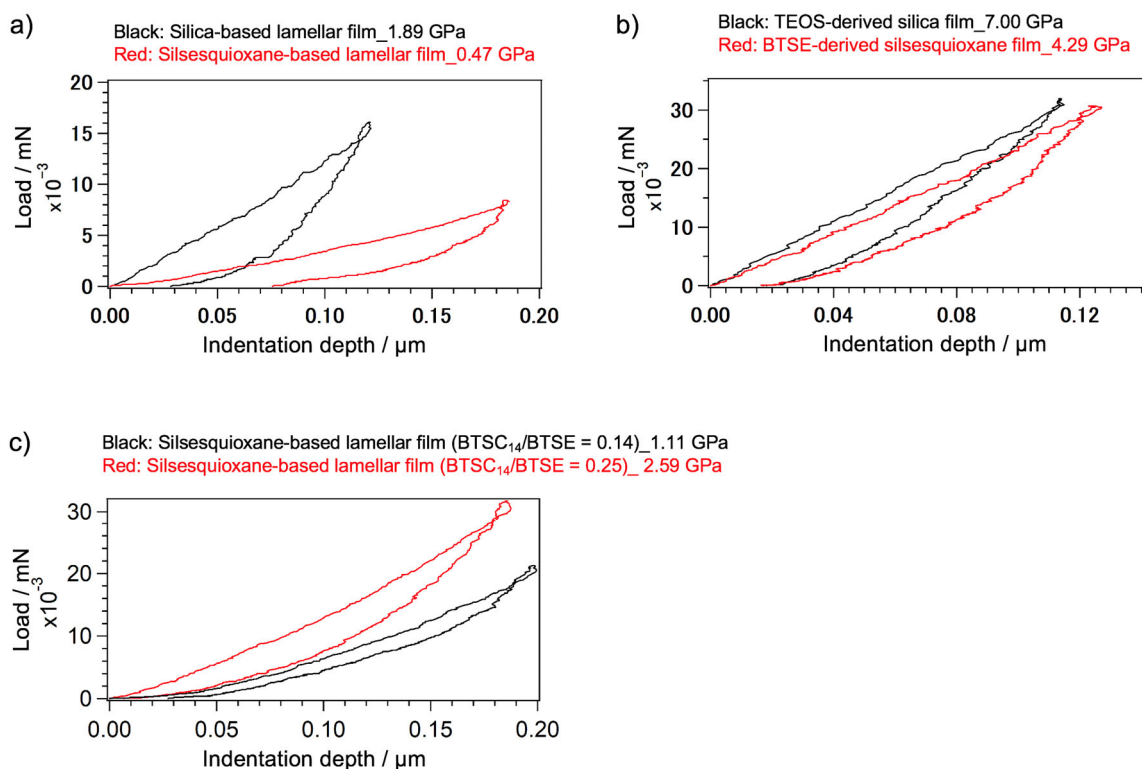


Figure S13 Nanoindentation load–displacement curves: (a) silica- and silsesquioxane-based lamellar films prepared using TEOS and BTSE, respectively, (b) surfactant-free silica and silsesquioxane films prepared using TEOS and BTSE, respectively, and (c) silsesquioxane-based lamellar films prepared at $\text{BTSC}_{14}/\text{BTSE} = 0.14$ and $\text{BTSC}_{14}/\text{BTSE} = 0.25$. The hardness was calculated by the Oliver–Pharr method (E. Broitman, *Tribol. Lett.*, 2017, **65**, 23).

The values of the hardness of the silica-based films are larger than those for similar films reported in our previous paper (S. Itoh et al., *ACS Nano*, 2017, **11**, 10289). This is because of the difference in the calculation methods. In our previous study, loading curves were only used for the calculation of the hardness because completely inelastic deformation occurred due to the high maximum loads. To obtain more accurate data, in Figure S13, indentation was performed at lower maximum loads so that elastic deformation could be observed, and the contact stiffness was calculated by differentiating the unloading curve fit.

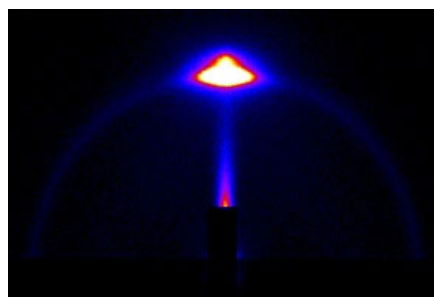
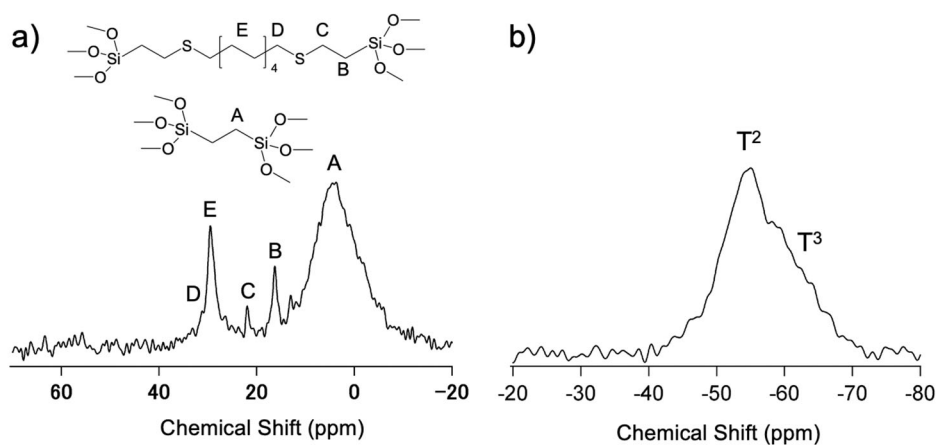


Figure S14 GI-SAXS pattern of the thin film prepared at $\text{BTSC}_{14}/\text{BTSE} = 0.14$. The measurement was performed at room temperature and 40% RH.



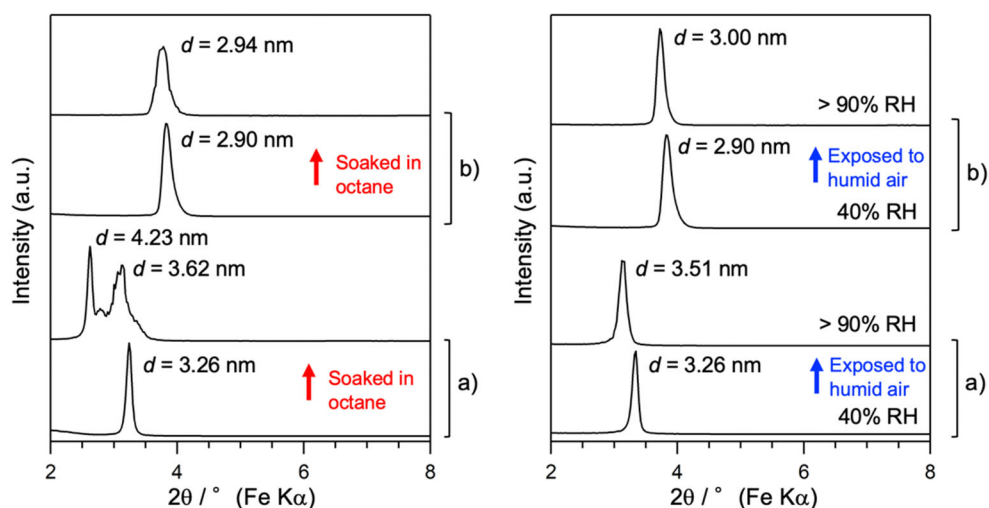


Figure S16 Left) XRD patterns of the silsesquioxane-based lamellar films prepared at (a) $\text{BTSC}_{14}/\text{BTSE} = 0$ and (b) $\text{BTSC}_{14}/\text{BTSE} = 0.14$ before and after being soaked in octane. Right) XRD patterns of the silsesquioxane-based lamellar films prepared at (a) $\text{BTSC}_{14}/\text{BTSE} = 0$ and (b) $\text{BTSC}_{14}/\text{BTSE} = 0.14$ before and after being exposed to humid air (>90% RH).

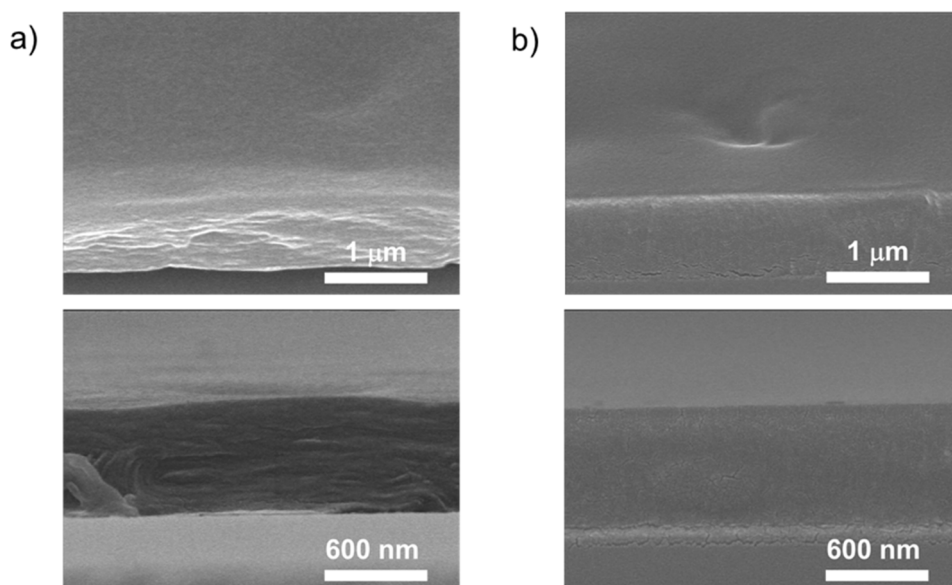


Figure S17 Cross-sectional SEM images of the fractured lamellar films prepared at (a) $\text{BTSC}_{14}/\text{BTSE} = 0$ and (b) $\text{BTSC}_{14}/\text{BTSE} = 0.14$.

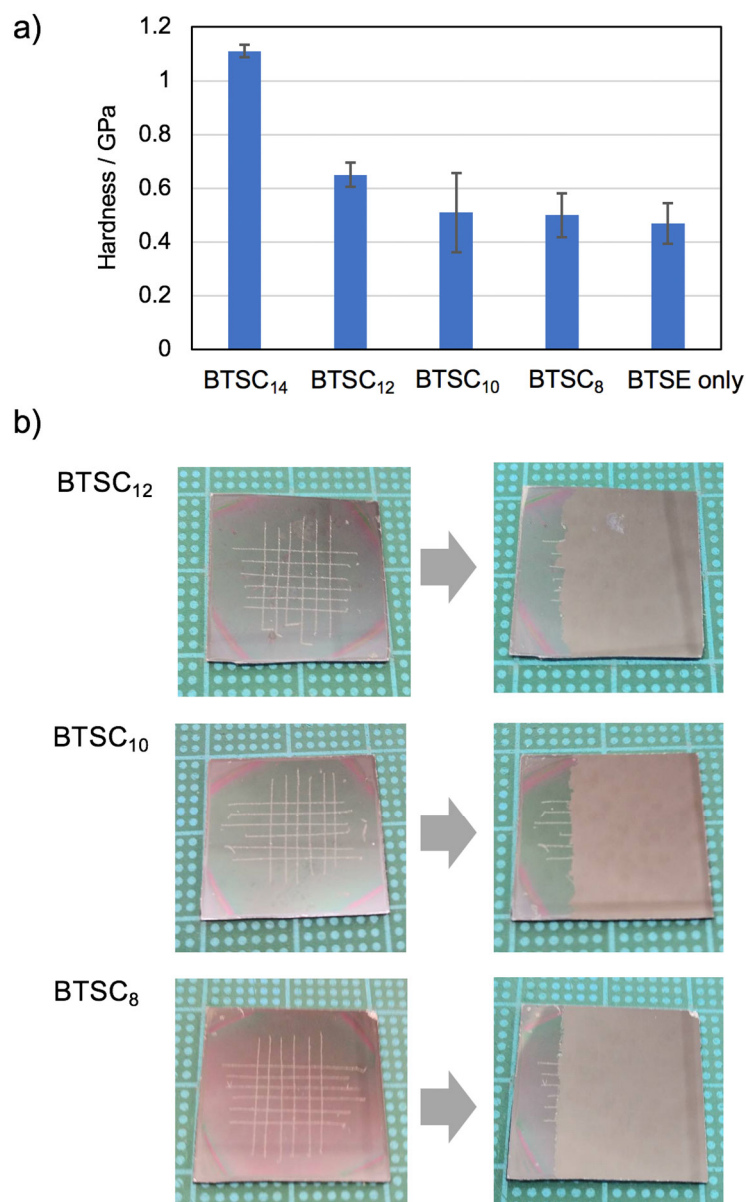


Figure S18 (a) Nanoindentation hardness for the lamellar films prepared from BTSC₁₄/BTSE, BTSC₁₂-BTSE, BTSC₁₀-BTSE, and BTSC₈-BTSE mixtures at BTSC_{*n*}/BTSE = 0.14 (*n* = 8–14). The hardness of the lamellar film prepared at BTSC₁₄/BTSE = 0 (BTSE only) is shown for comparison. (b) The results of Scotch tape testing for the lamellar films prepared from BTSC₁₂-BTSE, BTSC₁₀-BTSE, and BTSC₈-BTSE mixtures.

Movie S1 In situ observation of crack healing of the silsesquioxane-based lamellar film prepared using BTSE and DDAB. The cracks were formed by pressing a Knoop indenter on the film with a load of 490 mN at 23 °C and 52% RH. The cracks were observed by an optical microscope immediately after removal of the indenter.

Movie S2 In situ observation of lateral expansion of the silsesquioxane-based lamellar film upon exposure to humid air (>90% RH). The edge of the fractured film was observed by an optical microscope.

Movie S3 In situ observation of crack healing of the silsesquioxane-based lamellar film prepared using BTSE and DDAB on a flexible PDMS substrate. The cracks were formed by bending of the substrate. The film was exposed to humid air (>90% RH) during the optical microscopy observation.

Movie S4 In situ observation of crack healing of the silsesquioxane-based lamellar film prepared at $\text{BTSC}_{14}/\text{BTSE} = 0.14$. The crack was formed by pressing a Knoop indenter on the film with a load of 49 mN at 22 °C and 51% RH. The cracks were observed by an optical microscope immediately after removal of the indenter.

Movie S5 In situ observation of crack healing of the silsesquioxane-based lamellar film prepared at $\text{BTSC}_{14}/\text{BTSE} = 0.33$. The cracks were formed by pressing a Knoop indenter on the film with a load of 49 mN at 26 °C and 65% RH. The cracks were observed by an optical microscope immediately after removal of the indenter.