Electronic Supplementary Information

Multilayered organosiloxane films with self-healing ability converted from block copolymer nanocomposites

Yoshiaki Miyamoto,[a] Takamichi Matsuno,[a,b,c] and Atsushi Shimojima*[a,b,c]

a. Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.
b. Waseda Research Institute for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.
c. Kagami Memorial Research Institute for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan.

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1. Material

Acetonitrile (>99.9%) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; Allyl bromide (>98%) was purchased from Tokyo Chemical Industry Co., Ltd; Alumina, Activated was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; 1,2-bis(triethoxysilyl)ethane (BTSE, >96.0%) was purchased from Sigma-Aldrich; benzoyl peroxide (wetted with ca. 25% water) was purchased from Tokyo Chemical Industry Co., Ltd; chlorodimethylsilane (>95%) was purchased from Tokyo Chemical Industry Co., Ltd; ethanol (>99.5%) was purchased from Junsei Chemical Co., Ltd; 6 N HCl aq. was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; 1 N HCl aq. was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; 0.1 N HCl aq. was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; hydrogen hexachloroplatinate(IV) hexahydrate (>98.5%) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; Octamethylcyclotetrasiloxane (>98%) was purchased from Tokyo Chemical Industry Co., Ltd; Pluronic® P123 was purchased from Sigma-Aldrich; polydimethylsiloxane (PDMS), hydroxy terminated (*M*n = 550) was purchased from Sigma-Aldrich. PDMS, hydroxy terminated, (*M*w = 4200) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; polyethylene glycol monomethyl ether (average molecular weight: 1000) was purchased from Tokyo Chemical Industry Co., Ltd; potassium hydroxide was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; tetraethoxysilane (TEOS, >95%) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; tetrahydrofuran, stabilizer free (THF, >99.8%) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd; tetramethylammonium hydroxide (TMAOH) was purchased from Tokyo Chemical Industry Co.; toluene (>99.5%) was purchased from FUJIFILM Wako Pure Chemical Co., Ltd. These chemicals were used without further purification. Si (100) substrates were purchased from Silicon Technology.

2. Synthesis of PEO–PDMS–PEO

2.1 Synthesis of Ally-PEO

Potassium hydroxide (1.68 g, 0.03 mol), polyethylene glycol monomethyl ether (average molecular weight 1000, 6 g, 0.006 mol), and allyl bromide (5.08 g, 0.042 mol) were added to THF (50 mL), and the mixture was stirred at 80 °C for 2 d. After the reaction, precipitates were removed by filtration, and 6 N hydrochloric acid (0.01 mL) was added. Then, filtration was performed again, and the volatile components were evaporated to obtain a yellow solid. ^{1}H NMR (*d*, 500 MHz, $\mathrm{CDCl_3}$): 3.38 (s, 3H, $\mathrm{OC}H_3$), 3.5–3.8 (m, 96H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 4.02 (d, 2H, $\mathrm{CH_2CHC}H_2\mathrm{O}$), 5.22 (dd, 2H, $\mathrm{C}H_2\mathrm{CHCH_2O}$), 5.91 (m, 1H, $\mathrm{CH_2C}H\mathrm{CH_2O}$). *M*n, gel permeation chromatography (GPC) (chloroform) = 2130 g mol^{-1}, *M*w/*M*n = 1.09 relative to polyethylene glycol standards.

2.2 Synthesis of hydride-terminated PDMS (PDMS-H1and PDMS-H2)

Hydroxy-terminated PDMS (*M*n = 550, 10 g, 19.2 mmol) and chlorodimethylsilane (4.7 mL, 41.9 mmol) were reacted in THF (50 mL) by stirring at room temperature for 1 d. The solvent and HCl were removed under vacuum to give a clear viscous liquid (PDMS-H1). ^{1}H NMR (δ, 500 MHz, $\mathrm{CDCl_3}$): 0.05–0.12 (brs, 184H, $\mathrm{OSi(C}H_3)_2\mathrm{O}$), 0.185 (d, 12H,

$HSi(CH_3)_2O$) 4.71 (d, 2H, $HSi(CH_3)_2O$). *M*n, GPC (chloroform) = 1200 g mol^{-1}, *M*w/*M*n = 1.35 relative to polyethylene glycol standards. Similarly, hydroxy-terminated PDMS (*M*n = 4200, 20 g, 4.52 mmol) was reacted with chlorodimethylsilane (1.2 mL, 10.7 mmol) to obtain a clear viscous liquid (PDMS-H2). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 0.05–0.12 (brs, 408H, $OSi(CH_3)_2O$), 0.188 (d, 12H, $HSi(CH_3)_2O$) 4.71 (d, 2H, $HSi(CH_3)_2O$). *M*n, GPC (chloroform) = 3270 g mol^{-1}, *M*w/*M*n = 1.66 relative to polyethylene glycol standards.

2.3 Synthesis of PEO_{27}–$PDMS_{36}$–PEO_{27} and PEO_{27}–$PDMS_{82}$–PEO_{27}

In a Schlenk flask, a mixture of Allyl-PEO (2.62 g, 67.5 mmol), PDMS-H1 (1.2 g, 5 mmol), an acetonitrile solution of H_2PtCl_6 (0.05 mmol as Pt), and toluene (20 mL) was stirred under nitrogen atmosphere at 80 °C for 3 d. Solvent removal under reduced pressure, followed by the removal of unreacted Ally-PEO by GPC gave a clear viscous liquid (PEO_{27}–$PDMS_{36}$–PEO_{27}). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 0.05–0.1 (s, 210H, $OSi(CH_3)_2O$), 3.38 (s, 6H, OCH_3), 3.65 (s, 216H, OCH_2CH_2O). *M*n, GPC (chloroform) = 5400 g mol^{-1}, *M*w/*M*n = 1.25 relative to polyethylene glycol standards. Similarly, a mixture of Allyl-PEO (0.97 g, 25 mmol), PDMS-H2 (1.2 g, 0.23 mmol), an acetonitrile solution of H_2PtCl_6 (0.05 mmol as Pt), and toluene (20 mL) was stirred at 80 °C for 3 d. The removal of solvent and unreacted Ally-PEO gave a clear viscous liquid (PEO_{27}–$PDMS_{82}$–PEO_{27}). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 0.05–0.1 (s, 2600H, $OSi(CH_3)_2O$), 3.38 (s, 6H, OCH_3), 3.65 (s, 216H, OCH_2CH_2O). *M*n, GPC (chloroform) = 7030 g mol^{-1}, *M*w/*M*n = 1.47 relative to polyethylene glycol standards.

3. Preparation of lamellar thin film (**L1**) and the calcined film (**L2**)

Si substrates were washed with Semico Clean 23 (Furuuchi Chemical Co.) for 15 min and then in pure water for 15 min under ultrasonication. BTSE, P123, PEO_{27}–$PDMS_{36}$–PEO_{27}, EtOH, and HCl aq. were stirred for 1 h at room temperature at the molar composition of BTSE/P123/PEO_{27}–$PDMS_{36}$–PEO_{27}/EtOH/H_2O/HCl = 1:0.015:0.015:15:20:0.008. The resulting precursor solution (0.35 mL) was spin-coated at 3000 rpm for 30 s on a Si substrate (2 cm × 2 cm) at 25 °C and 40% relative humidity (RH), followed by air-drying at room temperature for at least 1 d. Note that P123 is necessary to form a lamellar structure at least under our experimental conditions. The prepared film (**L1**) was calcined in air in a muffle furnace to obtain **L2**. The temperature was raised from room temperature to 170 °C in 30 min and kept at 170 °C for 4 h.

4. Preparation of **L3** by treatment of **L2** with KOH

An aqueous solution of KOH (0.15 mol L^{-1}, 0.05 mL) was mixed with THF (20 mL). The solution was placed in a Petri dish, and the thin film (**L2**) was immersed for 1 d at room temperature. Then, the film was washed with THF and dried under reduced pressure for 1 d. For solid-state nuclear magnetic resonance (NMR) and Thermogravimetry–mass spectrometry (TG–MS) analyses, a powder sample of **L2** (0.04 g), which was prepared by drop-casting the precursor solution on substrates, followed by drying and pulverization, was immersed in a mixture of an aqueous solution of KOH (0.3 mol L^{-1}, 0.1 mL) and THF (8 mL) for 1 d at room temperature. The sample was recovered by filtration and dried at room temperature under reduced pressure for 1 d.

5. Preparation of multilayered silica-PDMS film

Si substrates were washed with Semico Clean 23 (Furuuchi Chemical Co.) for 15 min and then in pure water for 15 min under ultrasonication. TEOS, P123, PEO_{27}–$PDMS_{36}$–PEO_{27}, EtOH and HCl aq. were mixed at room temperature for 1 h at the molar composition of TEOS/P123/PEO_{27}–$PDMS_{36}$–PEO_{27}/EtOH/H_2O/HCl = 1:0.02:0.02:30:11.5:0.12. The resulting precursor solution (0.35 mL) was spin-coated at 3000 rpm for 30 s on a Si substrate (2 cm × 2 cm) at 25 °C and 40% RH. The prepared thin film was air-dried at room temperature for 1 d (**TEOS-1**). The prepared film was calcined at 200 °C for 4 h. The calcined film was immersed in a mixture of an aqueous solution of KOH (0.15 mol L^{-1}, 0.05 mL) and THF (20 mL) in a petri dish at room temperature for 1 d (**TEOS-3**).

6. Preparation of PDMS elastomers

PDMS elastomers with silanolate ends were synthesized following the previous report.[1,2]

6.1 Synthesis of **D_4-bisD_4**

Octamethylcyclotetrasiloxane (D_4) and 2.5 wt% benzoyl peroxide were mixed and stirred at 120 °C for 1 h under N_2 atmosphere. Activated alumina was added and the mixture was stirred at room temperature for 1 h. The mixture was then filtered to give a mixture of D_4 and 1.1 wt% bis(heptamethylcyclotetrasiloxanyl)ethane (bisD_4). ^1H NMR (d, 500 MHz, $CDCl_3$): 0.02–0.28 (m, 4300H, $OSi(CH_3)_2O$), 0.475(s, 4H, $Si(CH_2)_2Si$).

6.2 Preparation of elastomers

PDMS elastomers were prepared by mixing **D4-bisD4** and TMAOH.[1] **D4-bisD4** was mixed with a 25 wt% TMAOH aqueous solution and heated in the mold or on Si substrate at 90 °C for 1 d. The molar ratio of TMAOH to cyclic siloxane units was adjusted to

0.003, according to the previous report.[2]

7. Characterization

θ–2θ X-ray diffraction (XRD) patterns were collected in Bragg–Brentano geometry using Ultima IV diffractometer (Rigaku) with Fe Kα radiation (40 kV and 30 mA). Grazing-incidence small-angle X-ray scattering (GI-SAXS) patterns were collected in reflection mode using a NANO-Viewer (Rigaku) with Cu Kα radiation (40 kV and 30 mA) and a hybrid photon counting detector (Pilatus, Dectris) at 0.2° angle of incidence. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a JASCO FT/IR-6100 spectrometer in the transmission mode. Attenuated total reflection infrared (ATR-IR) spectra were obtained using a JASCO FT/IR-6100 spectrometer with attachment of a diamond prism. Liquid-state ^{1}H NMR spectra were obtained using a JEOL JNM-ECZ 500 spectrometer with resonance frequencies of 500.16 MHz at ambient temperature. The chemical shifts were referenced to internal tetramethylsilane at 0 ppm. Chloroform-*d* was used to obtain lock signals. GPC was carried out using a LaboACE LC-7080 recycling preparative HPLC system (Japan Analytical Industry Co., Ltd) equipped with a refractive index detector. JAIGEL-1HR and JAIGEL-2HR Plus were used as columns with chloroform as the eluent at a flow rate of 7.0 mL min^{-1}. The molecular weight and molecular weight distributions (Mw/Mn) of the polymers were measured by using a LC-NET II (Japan Analytical Industry Co., Ltd) using chloroform as the eluent (1.0 mL min^{-1}) and calibrated by polyethylene glycol standards. Solid-state ^{29}Si magic-angle spinning (MAS) NMR spectra were recorded on a JEOL JNM-ECX-400 spectrometer at a resonance frequency of 79.4 MHz with a 90° pulse and a recycle delay of 100 s. Solid-state ^{13}C MAS NMR spectra were recorded on the same spectrometer at a resonance frequency of 99.5 MHz with a pulse delay of 5 s. The samples were put in 4 mm zirconia rotors and spun at 5 Hz. The chemical shifts for solid-state ^{29}Si and ^{13}C NMR were referenced to polydimethylsilane at −33.8 ppm and hexamethylbenzene at 17.4 ppm, respectively. Scanning electron microscopy (SEM) images were taken using a Hitachi S5500 microscope at an accelerating voltage of 1 kV. Samples are dried at room temperature under reduced pressure for 1 d before observation. Cross-sectional scanning transmission electron microscopy (STEM) images were taken using a JEOL JEM-2100F microscope with an accelerating voltage of 200 kV. The distributions of Si, O, and C in the STEM images were recorded by energy-dispersive X-ray spectroscopy (EDS) using a Si (Li) detector in the high-angle annular dark field (HAADF) mode. The specimen was prepared using focused ion beam (FIB) milling (JEOL JIB-4000) to reduce the thickness to <100 nm after carbon-coating to protect the surface. The hardness of the film samples was calculated using a NEC San-ei Instruments MH4000 mechanical property tester attached with a triangular pyramidal indenter with an 80° face angle. The indentation speed was 2.7 nm s^{-1} and each sample was tested 10 times at different points. TG–differential thermal analysis (DTA) was conducted using a Rigaku Thermo plus EVO2 TG8121 under air flow (200 mL min^{-1}) at a temperature increase rate of 10 °C min^{-1}. α-Al_2O_3 was used as the standard sample, and an Al pan was used as the sample container. X-ray photoelectron spectroscopy (XPS) depth profile was recorded using VersaProbe II (ULVAC-PHI) using monochromated Al Kα radiation. Heights of the etched area were measured using BRUKER Dektak XT-S. TG–MS analysis was performed using ThermoMass (Rigaku) under N_2 atmosphere, and the temperature was increased at a ramping rate of 10 °C min^{-1}. α-Al_2O_3 was used as the standard sample, and an Al pan was used as the sample container.

8. Supplementary figures

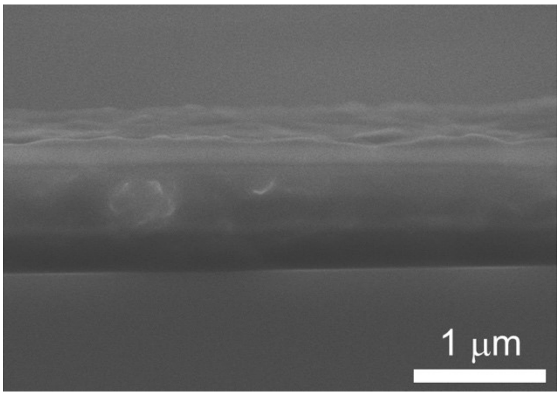

Fig. S1 Cross-sectional SEM image of **L1**. The film was broken off together with the Si substrate, and the fracture surface was observed without sputter coating.

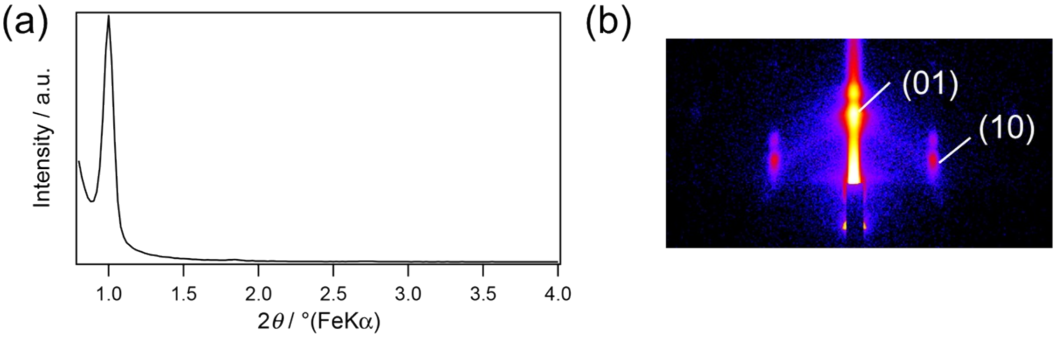

Fig. S2 (a) XRD pattern and (b) GI-SAXS pattern of the film prepared with a molar ratio of BTSE:P123:PEO_{27}–$PDMS_{36}$–PEO_{27} = 1:0.01:0.01. The outer scattered spots are attributed to the scattered spots derived from the specular reflection beam.

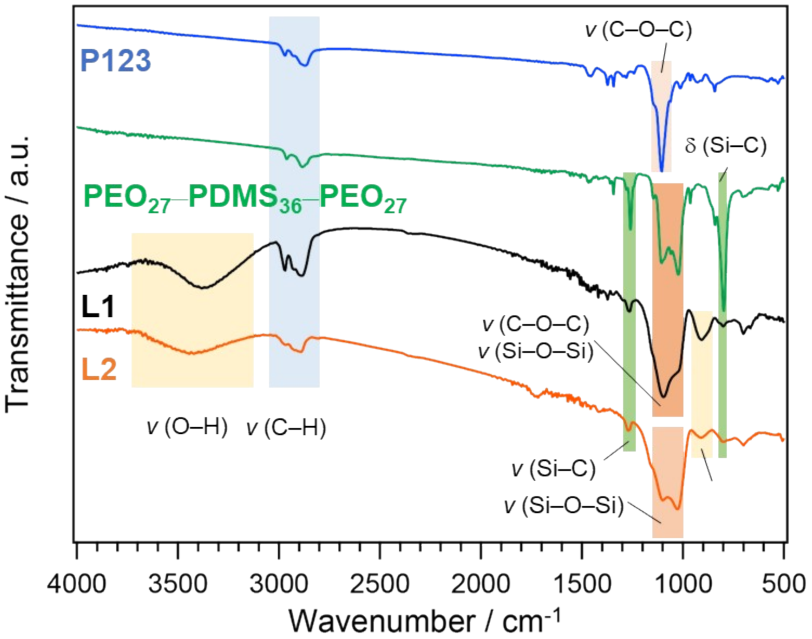

Fig. S3 FT-IR spectra of P123, PEO$_{27}$–PDMS$_{36}$–PEO$_{27}$, **L1**, and **L2**. THF solutions of P123 and PEO$_{27}$–PDMS$_{36}$–PEO$_{27}$ were spin-coated on Si substrates for the measurement.

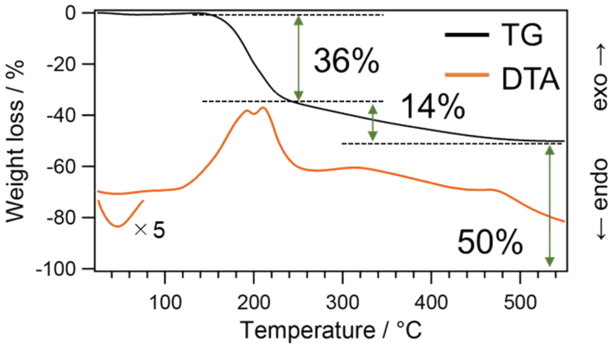

Fig. S4 TG–DTA curves of the powder sample of **L1** obtained by pulverizing the thick films prepared by drop-casting the precursor solution.

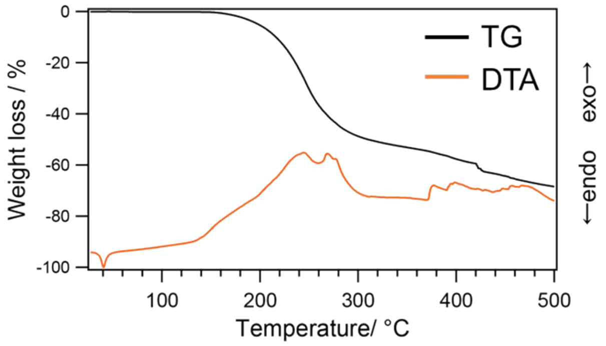

Fig. S5 TG–DTA curves of PEO_{27}–$PDMS_{36}$–PEO_{27}.

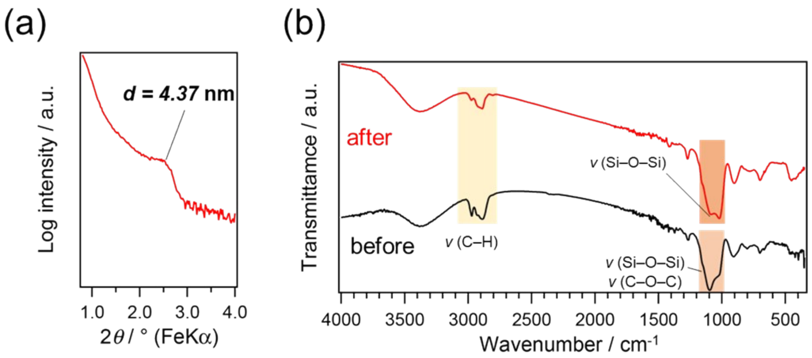

Fig. S6 (a) XRD pattern of **L1** after the removal of the block copolymers. (b) FT-IR spectrum of **L1** before and after the removal of the block copolymer. **L1** was stirred in a mixture of 6N HCl aq. (0.2 mL) and THF (10 mL) at room temperature for 10 min. Then, the film was washed with THF and dried in air.

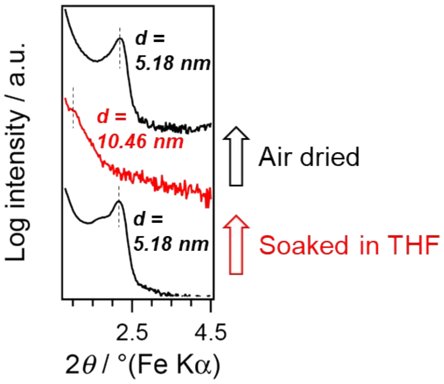

Fig. S7 XRD patterns of the thin film **L2** before and after soaking in THF.

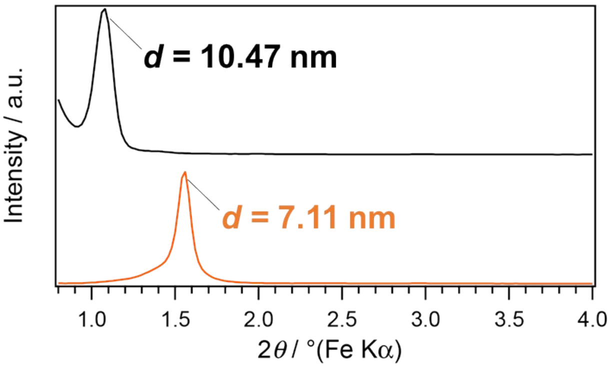

Fig. S8 XRD patterns of the lamellar film prepared using PEO$_{27}$-PDMS$_{82}$-PEO$_{27}$ (top) before and (bottom) after heating in air at 170 °C for 4 h.

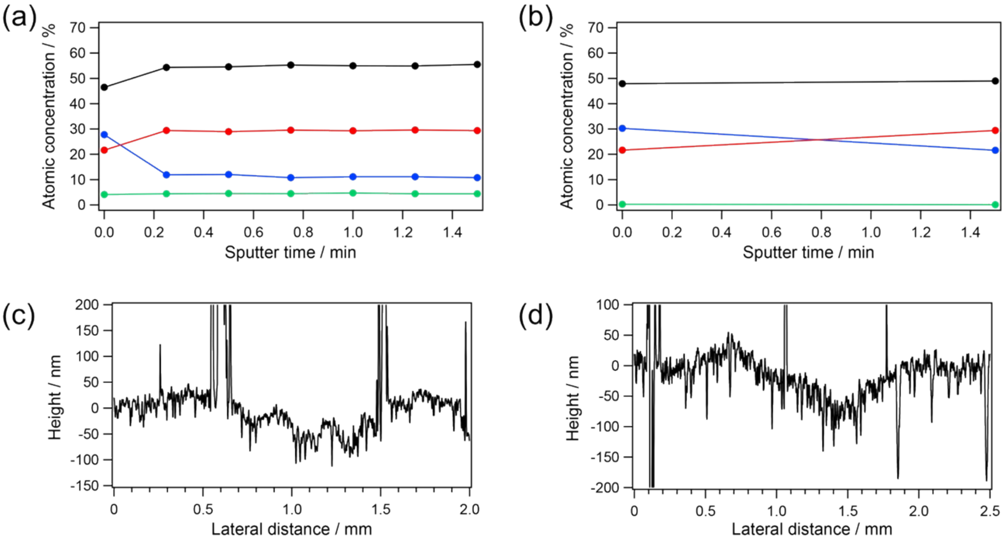

Fig. S9 (a, b) XPS depth profiles (by Ar etching) of the element distribution in the thin films of (a) **L3** and (b) **L2** (black: O, red: Si, blue: C, and green: K). (c, d) Surface height profiles of the etched areas of (c) **L3** and (d) **L2**.

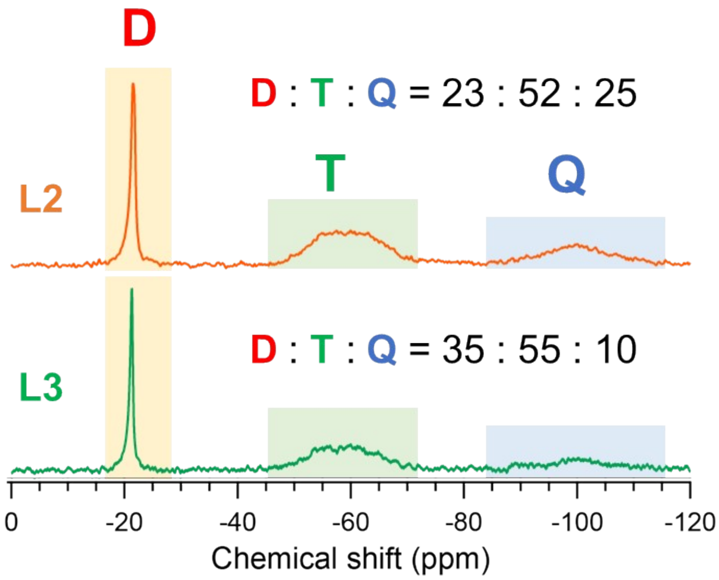

Fig. S10 Solid-state ^{29}Si MAS NMR spectra of the powder samples of (bottom) **L3** and (top) **L2** obtained by pulverizing the thick films prepared by casting the precursor solution. The relative intensity of the Q units (Q/(D + T + Q)) decreased after immersion in a KOH solution. This result is consistent with the previous finding that the dissolution rate of silica (Q siloxane) is much higher than that of silsesquioxane (T siloxane).[3] The T and D siloxanes with electron-donating organic groups are more stable against hydrolysis via the nucleophilic attack by OH$^-$.

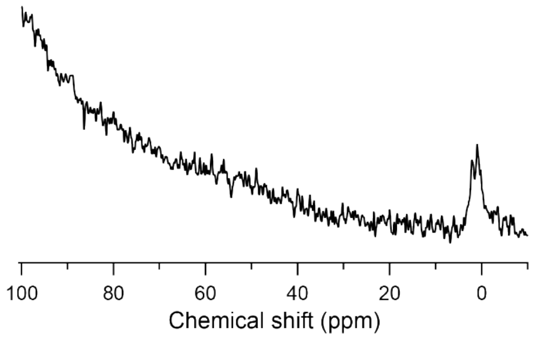

Fig. S11 Solid-state ^{13}C MAS NMR spectrum of **L3**.

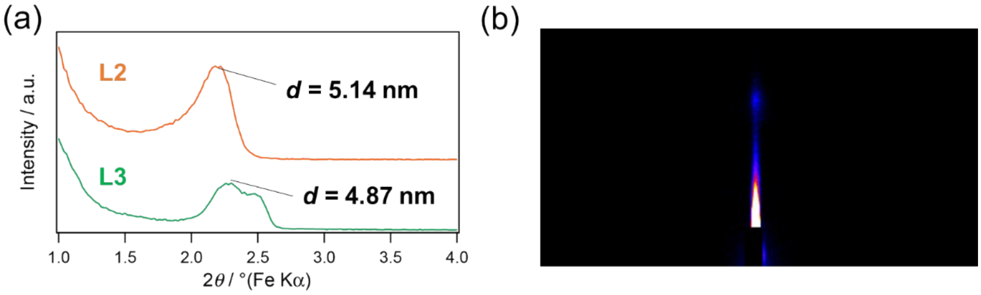

Fig. S12 (a) XRD patterns of **L3** and **L2**. (b) GI-SAXS pattern of **L3**.

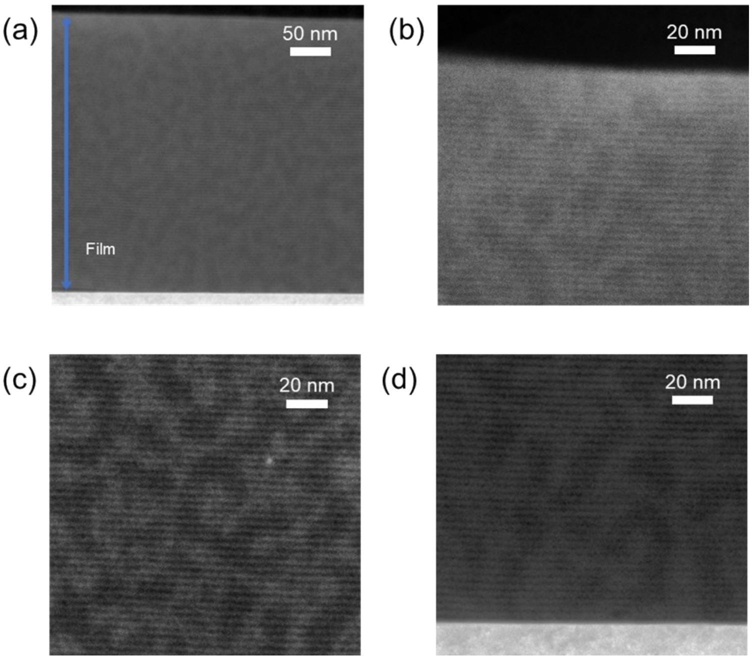

Fig. S13 (a) Cross-sectional HAADF-STEM images of **L3** cut vertically using FIB milling. (b, c, d) Magnified images near the film surface, in the middle of the film, and near the substrate, respectively. The periodicity of the layers (approximately 3.6 nm) was smaller than the *d* spacing, which may be due to the shrinkage of the film during FIB processing.

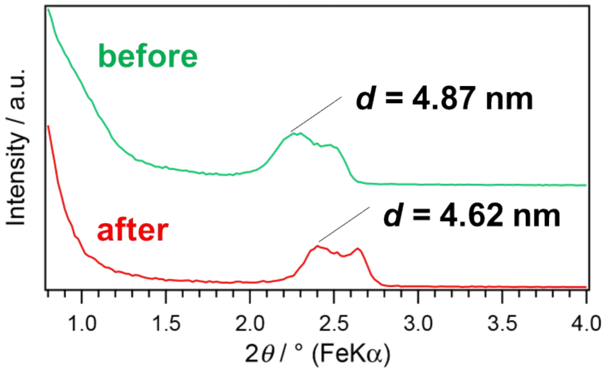

Fig. S14 XRD patterns of **L3** before and after treating the film at 80 °C and 40% RH for 1 d.

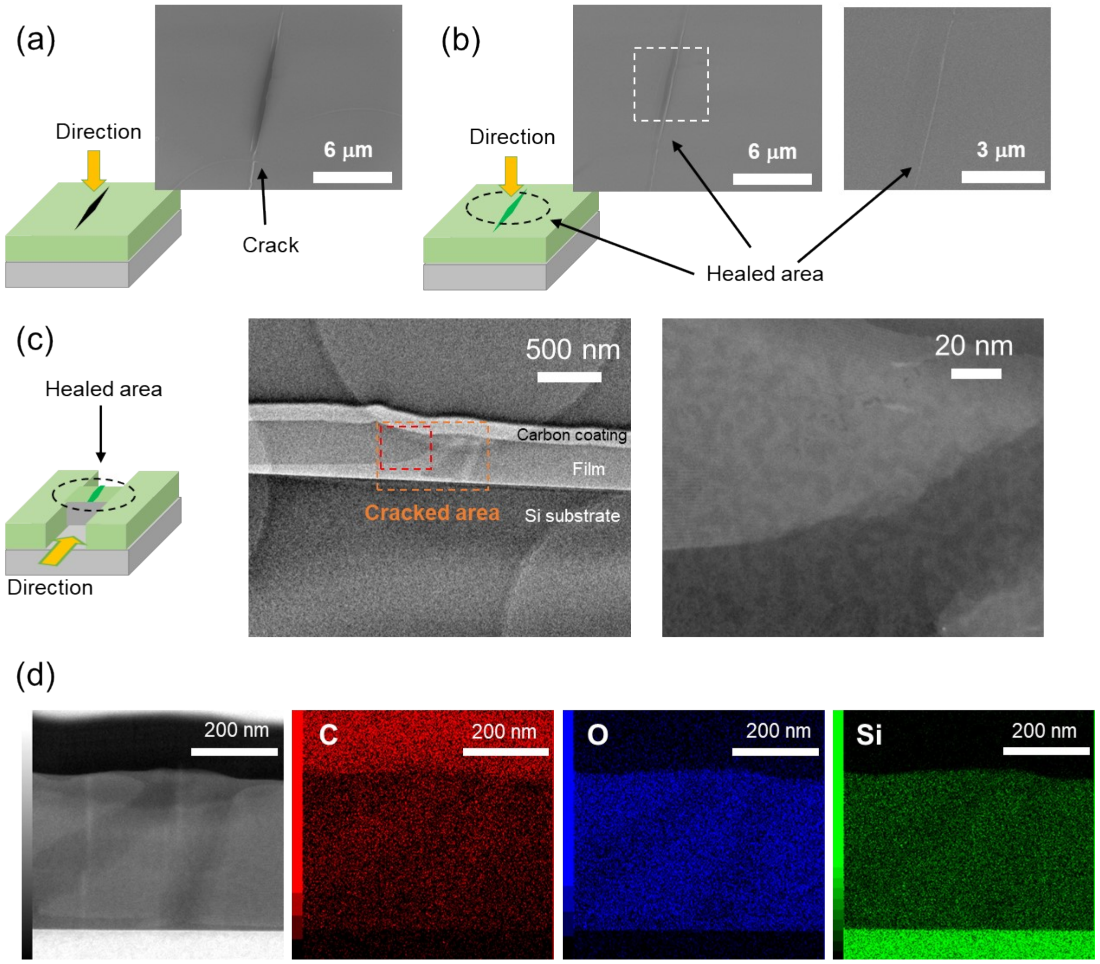

Fig. S15 SEM images of the crack on **L3** (a) before and (c) after the treatment at 80 °C and 40% RH for 1 d. (c) Cross-sectional TEM and HAADF-STEM images and (d) STEM-EDS mapping of the crack after the treatment at 80 °C and 40% RH for 1 d.

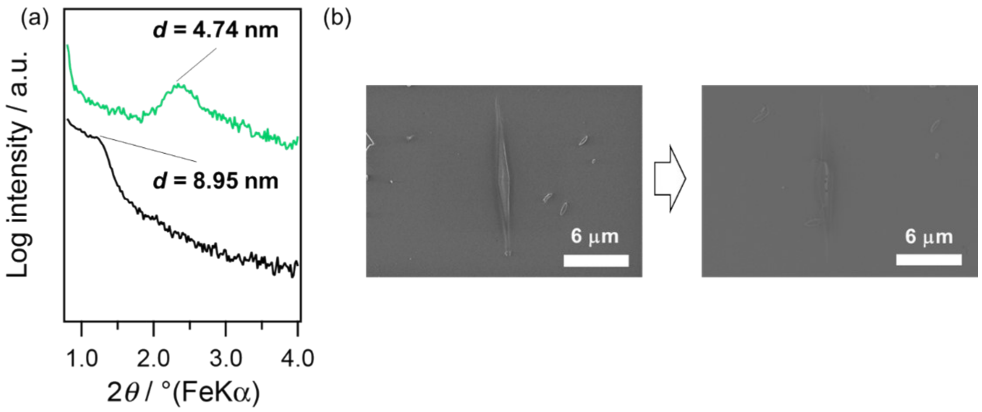

Fig. S16 (a) XRD patterns of (black) **TEOS-1** and (green) **TEOS-3**. (b) SEM images of the crack before and after the treatment at 80 °C and 40% RH for 1 d.

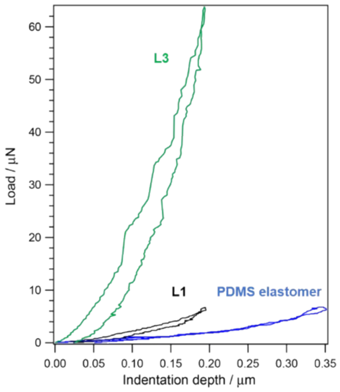

Fig. S17 Nanoindentation load–displacement curves of the lamellar thin film of **L1** and **L3** and PDMS elastomer. Hardness was calculated by the Oliver-Pharr method from the data obtained by continuously measuring the load and displacement during the process of pressing and unloading the triangular pyramidal indenter with an 80° face angle. In this report, we used an indenter with a shape factor of $g = 1.6$ and calculated the projected area of contact at the maximum load $A_{\mathrm{pml}} = gh_{\mathrm{c}}^2$ (h_{c} : contact depth). A constant value of $\varepsilon = 0.75$ was used for the calculation.

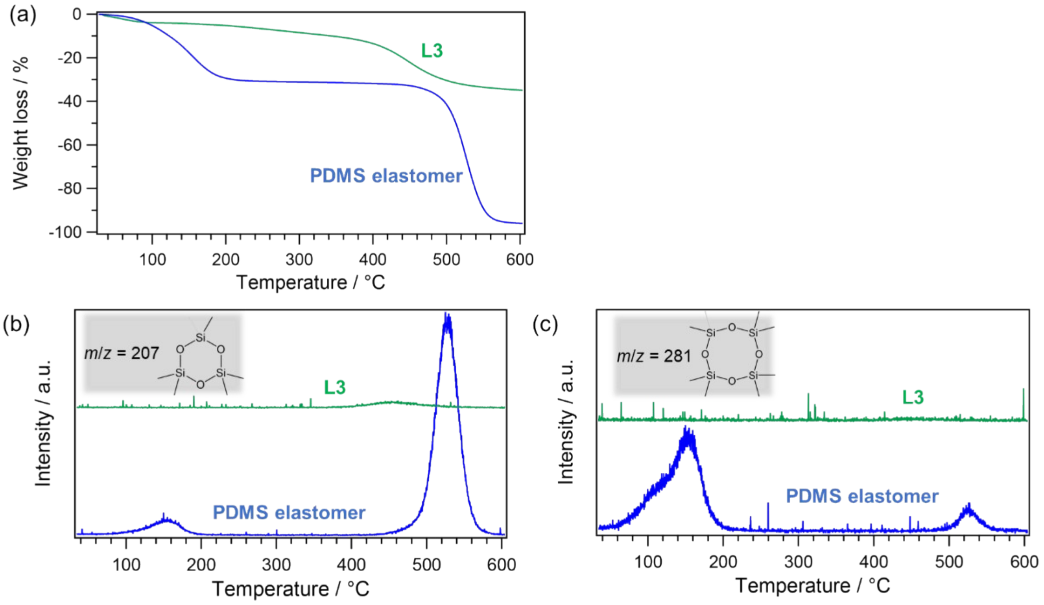

Fig. S18 TG–MS profiles of **L3** and PDMS elastomer. The gradual weight loss observed for **L3** in the low temperature range below 100 °C is probably due to the desorption of adsorbed water. The weight loss at higher temperature is likely caused by decomposition of the remaining PEO or PPO blocks and dehydration condensation of the residual silanol groups in the silsesquioxane layers.

References

1. W. Schmolke, N. Perner and S. Seiffert, *Macromolecules*, 2015, **48**, 8781–8788.
2. P. Zheng and T. J. McCarthy, *J. Am. Chem. Soc.*, 2012, **134**, 2024–2027.
3. N. Muramoto, T. Sugiyama, T. Matsuno, H. Wada, K. Kuroda and A. Shimojima, *Nanoscale*, 2020, **12**, 21155–21164.