Supporting Information

A Thermally Stable, Durable and Temperature-Dependent Oleophobic Surface of a Polymethylsilsesquioxane Film

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Experimental

Materials

0.01 M hydrochloric acid (HCl), ethanol (EtOH), *n*-hexadecane, *n*-dodecane, and *n*-decane were purchased from Wako Pure Chemical Industries Ltd. Methyltriethoxysilane (MTES) and tetramethoxysilane (TMOS) were purchased from Tokyo Kasei Kogyo. Co. Ltd. Phenylmethylsiloxane homopolymer (PMM, Figure S1) and *n*-decyltriethoxysilane (C_{10}TES) were purchased from Gelest Inc. *M*-bis(m-phenoxyphenoxy)benzene (5P4E, Figure S1) was purchased from MORESCO Co. All chemicals are used as received.

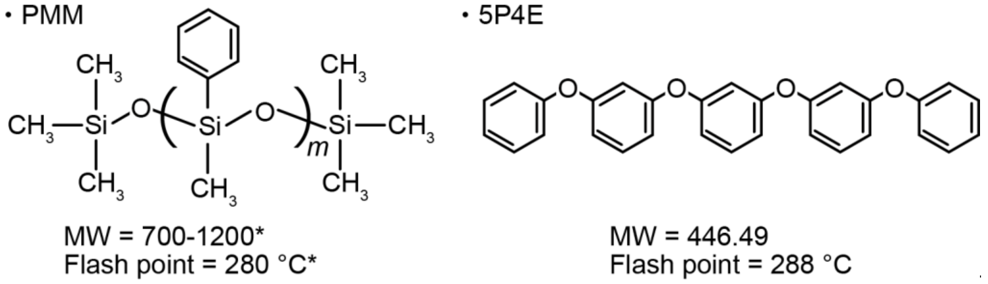

Figure S1. Chemical structures of PMM and 5P4E (* data from manufacture).

Sample preparation

Preparation of polymethylsilsesquioxane (PMSQ) films

PMSQ film was prepared through an acid catalyzed sol-gel reaction. MTES was first hydrolyzed and condensed in the 0.01M HCl (aq.)/ethanol solution for 24 h at room temperature. This precursor solution was then spin-coated (500 rpm for 5 sec and 2000 rpm for 10 sec, 25 °C, < 10 % RH) directly on glass slides (24×48 mm^2), polyimide (Kapton®, 24×78 mm^2), and stainless-steel (SUS 304) substrates (SUS, piece (20×20 mm^2 and 20×100 mm^2) and disk (ϕ50 mm) without any pretreatment and subsequently dried in an oven maintained at 100 °C for 24 h to promote condensation of siloxane networks. This sample is referred to as an initial PMSQ in this paper. Without this thermal treatment, the films are not substantially solidified after drying at room temperature (several weeks were required for solidification). The typical molar ratio of the precursor solution was MTES/EtOH/H_2O/HCl = $1:7:1.5:2.7\times10^{-4}$. For comparison, C_{10}-hybrid films are coated on the glass slide according to our previous reports. The typical molar ratio of the precursor solution for C_{10}-hybrid was C_{10}TES/TMOS/EtOH/H_2O/HCl = 1:9:90:40:0.02.

Characterization

Contact angles (CAs) were measured with a CA meter (Kyowa Interface Science CA-V150). Static (θ_S) and dynamic (advancing θ_A and receding θ_R) CAs were collected using several probe liquids (*n*-hexadecane, *n*-dodecane, *n*-decane, 5P4E, and PMM) at a determined temperature between 25 and 280 °C. For θ_S measurements, probe liquids (3 μL) were placed gently on the samples. For dynamic CA measurements, about 3 μL of probe liquid droplets (*n*-hexadecane, *n*-decane, and *n*-dodecane) were added and withdrawn from the surface, respectively. CA data reported here were determined by averaging values measured at five different points on three different samples (n = 3) under the same preparation conditions. Minimum tilt angles (TAs) needed to set probe liquid droplets (5 μL for *n*-hexadecane, *n*-decane, *n*-dodecane, 5P4E, and PMM) in motion on the samples were measured using a custom-made TA meter at a determined temperature (25-280 °C). Surface tensions of probe liquids were measured by the hanging drop method (Kyowa Interface Science DM-701). The film thicknesses of the samples were measured by a stylus profiler (Veeco Dektak 6M). UV-vis spectra were recorded with a Cary 5000 spectrophotometer (Agilent Technologies Inc.). The morphology of the samples was observed by atomic force microscopy (AFM) with optical microscopy (VN-8000, Keyence Co.). Viscosities of probe liquids were estimated using Oil-Power Viscosity Temperature Calculator based on the ASTM D341 equation.

Durability/stability tests in water, acid and base solutions

Some of the PMSQ-coated samples were submerged in Milli-Q water, a 0.01M HCl or 0.01 M NaOH solution, respectively, for a maximum of 10 min under shaking condition (100 rpm). After immersion, the samples were immediately washed with Milli-Q water several times and blown dry with N_2 gas. Changes in liquid-repellency of the samples were evaluated by measuring θ_s, θ_A/θ_R and CA hysteresis ($\Delta\theta_{cos} = \cos\theta_R - \cos\theta_A$) using alkanes (*n*-hexadecane, *n*-dodecane and *n*-decane) as probe liquids.

Thermal durability tests

(A) Thermal durability test under dry conditions

PMSQ-coated samples were treated inside a furnace installed with a programmable temperature controller. Its temperature was increased to a pre-determined temperature between 150 and 400 °C within 1 h, and then remained there for 24 h. The samples were then removed from the furnace and cooled spontaneously down to room temperature. Changes in liquid-repellency of the samples were evaluated by measuring θ_S, θ_A/θ_R, CA hysteresis ($\Delta\theta_{cos} = \cos\theta_R - \cos\theta_A$) and substrate TAs using alkanes (*n*-hexadecane, *n*-dodecane and *n*-decane) as probe liquids.

(B) *In-situ* thermal durability tests

Three different tests were conducted to estimate the *in-situ* thermal durability of our films. Here, we used SUS as a substrate due to its excellent thermal shock resistance. In this case, the PMSQ-coated SUS plate treated at 300°C for 1 h in advance was employed to exclude thermal history on the PMSQ films.

(B-1) Investigation of dewettability of PMSQ coating on the heated substrates

The first durability test was performed by heating the PMSQ-coated substrate (SUS, 20 × 20 mm^2) from 25 to 280 °C (for 5P4E) and to 230 °C (for PMM), respectively, using thermally stable probe liquids as shown in Figure S1. Changes in θ_S and TAs of these probe liquids at a determined substrate temperature were evaluated by using the custom-made heating stage. Probe liquid drops (3 μL for θ_S and 5 μL for TA) were set on the heating stage and heated to a determined temperature for 10 min to stabilize the temperature before each measurement.

(B-2) Thermal stress test

In the second durability test, changes in θ_S of PMM liquid of an identical sample were monitored after a dozen times of thermal-stress tests between 25 °C and 230 °C.

(B-3) Thermal durability test under wet conditions

Our third test was demonstrated as follows. The PMSQ-coated SUS disk (ϕ50 mm) was first set in the rotor and then the disk was semi-submerged in the oil bath filled with 5P4E, as shown in Figure S2. The disk was then rotated at 5 rpm and subsequently the oil bath was heated gradually and maintained at approximately 250°C in air for 30 h. We stopped the latter test after 30 h for safety, because 5P4E starts to degrade after 30h.

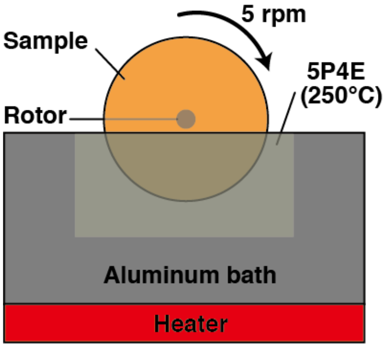

Figure S2. Schematic illustration of an experimental setup for thermal durability test of PMSQ film under wet conditions.

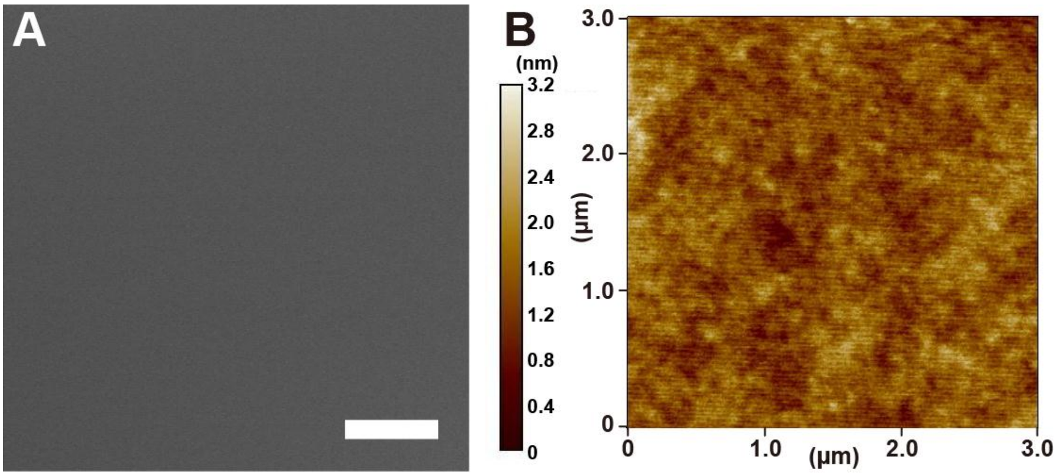

Figure S3. **(**A) Typical SEM (Scale bar = 10 μm) and (B) AFM images of the PMSQ-coated glass slide.

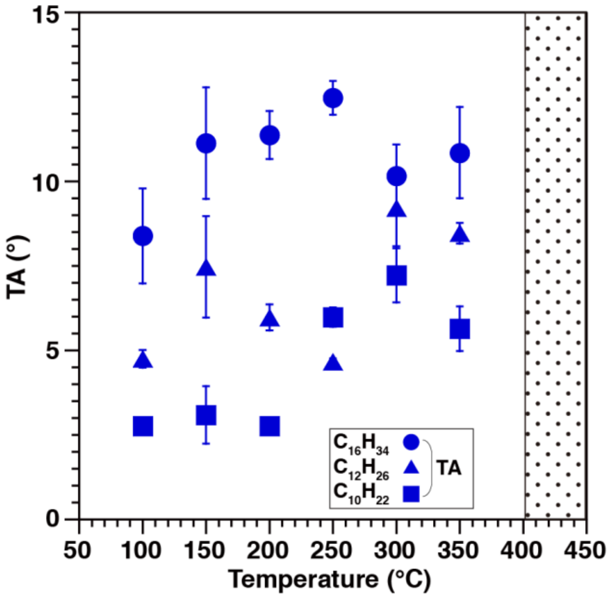

Figure S4. Substrate TAs of PMSQ-coated glass slide for *n*-hexadecane, *n*-dodecane, and *n*-decane as a function of thermal treatment under dry conditions.

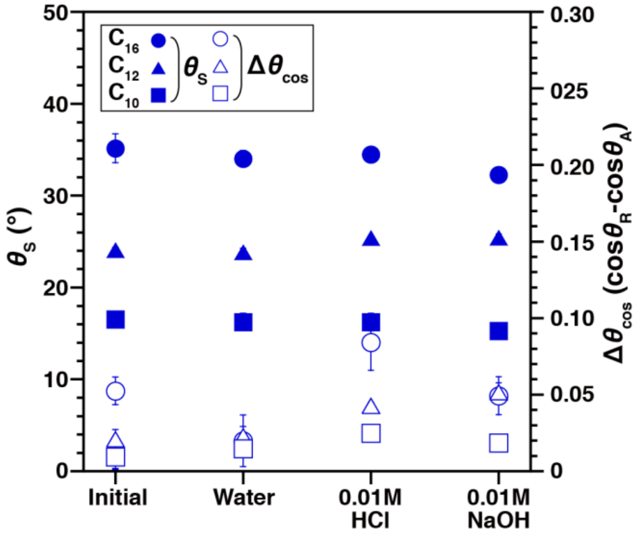

Figure S5. Changes in static and dynamic CAs for *n*-hexadecane, *n*-dodecane, and *n*-decane on C_{10}-hybrid-coated glass slide after immersion into Milli-Q water, a 0.01M HCl or 0.01 M NaOH solution for 10 min.

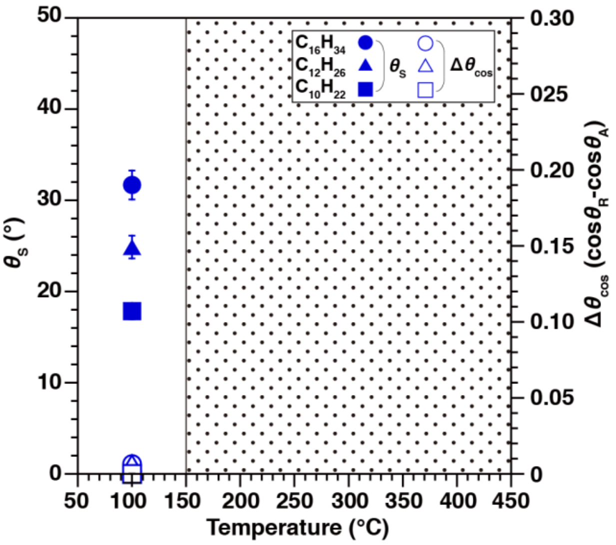

Figure S6. Changes in static and dynamic CAs for *n*-hexadecane, *n*-dodecane, and *n*-decane on C_{10}-hybrid-coated glass slide after thermal treatments at different temperatures. The surface oleophobicity disappeared completely after the thermal treatment above 150 °C (dot area).

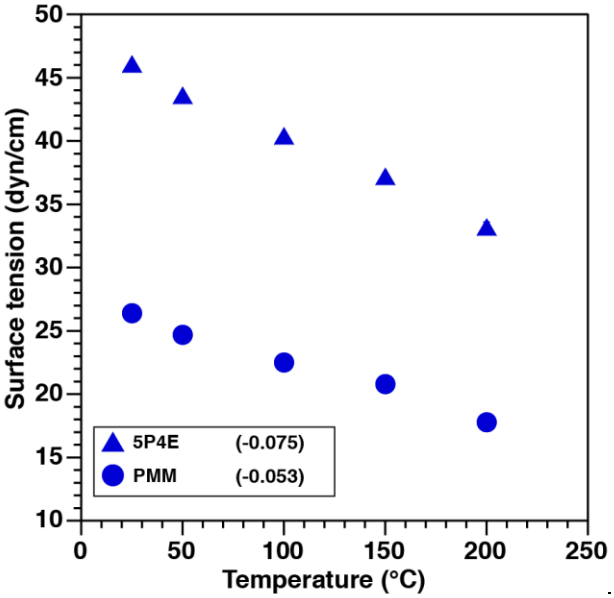

Figure S7. Temperature dependence of surface tension for each probe liquid. Numbers in the bracket indicate the temperature coefficients of temperature-dependent surface tension (dγ/dT).

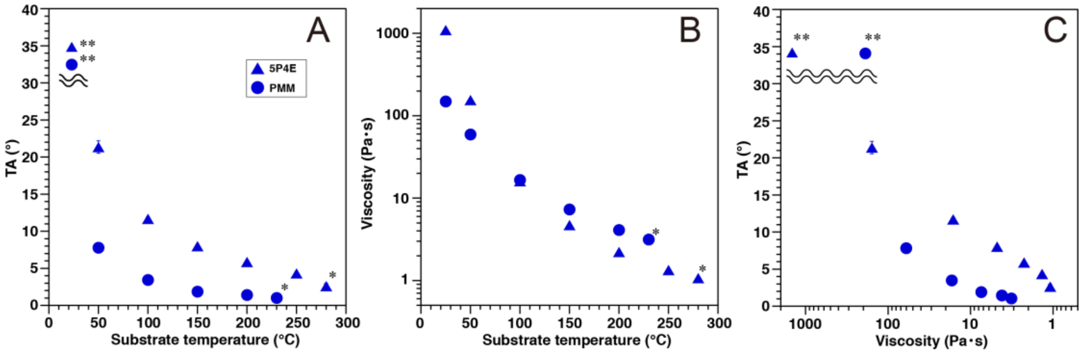

Figure S8. Changes in (A) substrate TAs and (B) viscosity with substrate temperature and (C) TAs with viscosity of probe liquids on a PMSQ-coated stainless steel for two probe liquids (*maximum temperature of probe liquids and ** more than 90°).

Movie S1. Transformation of a PMM droplet induced by the elevation of substrate temperature by heating of PMSQ-coated SUS piece (4× faster).

Movie S2. Appearances of PMSQ-coated SUS disk semi-submerged in 5P4E oil (16× faster).