Supplementary Information (SI)

Preparation of highly thermally stable and soluble ethylene-crosslinked ladder-like polymethylsiloxanes via template polymerisation

Sho Nonaka,[a] Kazuhiro Shikinaka,[b] Tomoyasu Hirai,[c] and Yoshiro Kaneko*[a]

[a.] *Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan.*

[b.] *Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), Nigatake, 4-2-1, Miyagino-ku, Sendai, Miyagi 983-8551, Japan.*

[c.] *Faculty of Engineering, Osaka Institute of Technology, 5-16-1 Omiya, Asahi-ku Osaka 535-8585, Japan.*

*To whom correspondence should be addressed (Tel: +81-99-285-7794, FAX: +81-99-285-7794, E-mail: ykaneko@eng.kagoshima-u.ac.jp)

Experimental section

Materials. 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisiloxane (purity: ~95.0%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, purity: ~98.0%), chlorotrimethylsilane (CTMS, purity: ~98.0%), diethoxymethylsilane (DEMS, purity: ~95.0%), platinum(0)-1,3-divinyltetramethyldisiloxane complex (Karstedt's catalyst, purity: 19.0–21.5% as platinum content, containing 1,3-divinyltetramethyldisiloxane), diethoxymethylvinylsilane (DEMVS, purity: ~97.0%), tris(2,4 pentanedionato)chromium(III) ($Cr(acac)_3$, purity: ~98.0%) and tetramethylsilane (TMS, purity: ~99.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Dichloromethane (DCM, purity: ~99.5%), tetrahydrofuran (THF, purity: ~99.5%), purified water (purity: unknown), benzoic acid (purity: ~99.5%), pyridine (purity: ~99.5%), acetonitrile (purity: ~99.5%), diethyl ether (purity: ~99.5%), xylene (a commercial mixture containing *ca*. 80% *o*-, *m*- and *p*-xylene and *ca*. 20% ethylbenzene), molecular sieves 3A 1/16, toluene (purity: ~99.0%), *N*,*N*-dimethylformamide (DMF, purity: ~99.5%), hydrochloric acid (HCl, purity 35.0–37.0%), methanol (purity: ~99.5%), *n*-hexane (purity: ~95.0%), chloroform (purity: ~99.0%), dimethyl sulfoxide (DMSO, purity: ~99.0%), acetone (purity: ~99.0%), 2,6-dimethyl-4-heptanone (purity: ~90.0%), ethyl acetate (purity: ~99.5%), 1-propanol (purity: ~99.5%), 1-butanol (purity: ~99.0%), chloroform-*d* (purity: 99.8%, with and without 0.05% TMS) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. Ethanol (purity: ~99.5%) was purchased from Japan Alcohol Trading Co., Ltd. A poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline), polyamic acid solution (Pyre-M.L.® RC-5069, ~12.8% solid content, solvent: 80% *N*-methyl-2-pyrrolidone/20% aromatic hydrocarbon) and cage octamethylsilsesquioxane (Me-POSS, purity: unknown) were purchased from Sigma-Aldrich Co., LLC. Activated carbon powder (particle size: ~20 μm) was purchased from Kanto Chemical Co., Inc. A silicone elastomer kit (Sylgard 184) was obtained from Dow Inc.

Measurements. Proton and silicon nuclear magnetic resonance (^{1}H and ^{29}Si NMR) spectra were recorded using an ECX-400 spectrometer (JEOL RESONANCE Inc., Tokyo, Japan). The weight-average molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined via gel permeation chromatography (GPC) using polystyrene standards. This GPC analysis was performed using SHIMADZU CTO-20AC and a SHIMADZU RID-20A (Shimadzu

Corporation, Kyoto, Japan) with Shodex KF-803L (bead size: 6 μm, measurable molecular weight range: 1.0×10^2–7.0×10^4) and Shodex KF-805L (bead size: 6 μm, measurable molecular weight range: 1.0×10^2–5.0×10^6) columns. THF was used as the eluent, with a flow rate of 1.0 mL min^{-1} at 40°C. Transmission electron microscopy (TEM) was performed using a JEM-2100 plus transmission electron microscope equipped with a LaB_6 source (JEOL Ltd., Tokyo, Japan) and operated at an acceleration voltage of 200 kV. TEM images were recorded using a 3,072 × 3,072 pixel Rio 9 CMOS camera (Gatan Co., Ltd., USA). A 1.0 wt% *n*-hexane solution of ECL–LPMS–TMS was prepared, and 10 μL of this solution was dropped onto an elastic carbon grid (Okenshoji Co., Ltd.). After resting for 10 s, the solution was absorbed using filter paper and dried. Wide-angle X-ray diffraction (WAXD) measurements were performed on the BL40B2 beamline at the SPring-8 facility in Hyogo, Japan. X-ray wavelength (λ) was set to be 0.1 nm. The diffraction was detected using PILATUS3 2M (253. 7 mm × 288.8 mm with a pixel size of 172 μm × 172 μm). The distance between the sample to the detector was calibrated with silver behenate standard and fixed at 491 mm. Scattering vector (**q**) is defined as $\mathbf{q} = (4\pi/\lambda)\sin\theta$. Where θ is Bragg angle. Thermogravimetric analysis (TGA) was performed using TGA-50 (SHIMADZU Co., Kyoto, Japan). Samples were preheated at 120°C for 30 min under nitrogen flow (100 mL min^{-1}) to remove residual solvent. After cooling to room temperature (*ca*. 25°C), the samples were heated to 1000°C at a heating rate of 10°C min^{-1} under nitrogen flow (100 mL min^{-1}). Differential scanning calorimetry (DSC) analysis was performed using DSC-60 Plus (SHIMADZU Co., Kyoto, Japan). Each sample was placed in an aluminum capsule and cooled to −150°C at a rate of 20°C min^{-1} under a nitrogen flow (50 mL min^{-1}). It was then heated from −150°C to 250°C at the same rate. The third heating curve (from −150°C to 250°C at a rate of 20°C min^{-1}) was used as the data to eliminate heat history effects from the samples. Ultraviolet–visible (UV–Vis) spectra were recorded using a JASCO V-630 spectrophotometer.

Preparation of PMVS–TMS (Schemes 1a and b). PMVS–TMS, a precursor for ECL–LPMS and ECL–LPMS–TMS, was prepared following a previously reported methodology.[34] First, 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane (13.61 g, 50.0 mmol) was dissolved in DCM (16 mL). TBD (0.071 g, 0.50 mmol), used as a catalyst, was dissolved in THF (12 mL) and added to the DCM solution, which was stirred for *ca*. 1 min. Purified water (90.0 μL, 5.0 mmol) was added while stirring the mixture. The reaction mixture was stirred at 30°C for 3 h, after which benzoic

acid was added to neutralize the reaction solution to pH 7. This neutralization was monitored using pH test paper. The reaction solution was poured into acetonitrile (600 mL) and stirred at room temperature for *ca*. 1 h. The acetonitrile-insoluble portion was isolated by decantation, and the procedure was repeated with acetonitrile volumes reduced to 400, 200 and 100 mL. Finally, the acetonitrile-insoluble portion was recovered and dried under reduced pressure, affording PMVS with terminal Si–OH groups as a colorless and transparent viscous liquid. The terminal Si–OH groups were then protected using a silylating agent, as described further. Pyridine (3.164 g, 40.0 mmol) and CTMS (3.430 g, 30.9 mmol) were added to the entire amount of prepared PMVS, and the mixture was stirred at 30°C for 50 min. The reaction solution was then poured into acetonitrile (300 mL) and stirred at room temperature. Similar to the previous step, the acetonitrile-insoluble portion was isolated by decantation, and the procedure was repeated with acetonitrile volumes reduced to 300 and 200 mL. Finally, diethyl ether (~10 mL) was added to the acetonitrile-insoluble portion to dissolve and recover it. The solution was concentrated using an evaporator and dried under reduced pressure, yielding PMVS–TMS as a colorless and transparent viscous liquid (5.962 g, yield 46%, calculated using the ideal chemical formula for the repeating unit of PMVS–TMS [$SiO(CH_3)(CH{=}CH_2)$, FW = 86.16]). GPC analysis revealed that the M_w and M_w/M_n values of PMVS–TMS were 9.6×10^3 and 1.28, respectively (Fig. 1a). The average degree of polymerization (DP) of PMVS–TMS was calculated to be 109 based on its M_w and FW of the repeating unit ([9.56×10^3 – 162.38 (FW for trimethylsilyl group)]/86.16). Additionally, in the ^{1}H NMR spectrum in $CDCl_3$ (Fig. 2a), the average DP was calculated to be 90 [(b/3H)/(a/18H)] based on the integral ratio of signal a to the signal b, which correspond to the trimethylsiliyl end groups and the methyl groups in the repeating units, respectively. ^{1}H NMR (400 MHz, $CDCl_3$, Fig. 2a): δ 6.04–5.89 (m, 2H, –$SiO(CH_3)(CH{=}C\mathit{H}_2)$), 5.83–5.75 (m, 1H, –$SiO(CH_3)(C\mathit{H}{=}CH_2)$), δ 0.16–0.13 (s, 3H, –$SiO(C\mathit{H}_3)(CH{=}CH_2)$), δ 0.09 (s, 9H, – $Si(C\mathit{H}_3)_3$). ^{29}Si NMR (79.4 MHz, $CDCl_3$, Fig. 3a): δ 8.70–8.17 (M), δ −33.9–−36.0 (D^2).

Preparation of ECL–LPMS (Schemes 1c and d). A diluted Karstedt's catalyst solution (2.1 mL, 3.1×10^2 mol L^{-1}) was prepared by mixing 0.638 g (0.654 mmol platinum) of commercially available Karstedt's catalyst solution (20% platinum content) with 1.714 g of dehydrated xylene. PMVS–TMS (0.143 g, 1.64 mmol vinyl groups) and DEMS (0.243 g, 1.72 mmol) were mixed in dehydrated xylene (1.5 mL), followed by the addition of the diluted Karstedt's catalyst solution

(0.311 mol L^{-1}, 133 μL, 41.3 μmol platinum). The solution was stirred at *ca*. 30°C in an argon atmosphere. Upon completion of the reaction, 0.017 g of activated carbon powder was added to the solution, which was then stirred for 1 h under an argon atmosphere in an ice bath (~4°C). The activated carbon powder was then removed by filtration, and the resulting solution was added to a mixed solvent of toluene (600 mL) and DMF (400 mL). Purified water (312 μL, 17.3 mmol) and concentrated hydrochloric acid (278 μL, 3.28 mmol) were then added to the solution. This solution was stirred at 120°C for 72 h under reflux. It was then concentrated to *ca*. 10 mL using a rotary evaporator at ~80°C, poured into purified water (350 mL), and stirred at room temperature. The water-insoluble portion was isolated by filtration, and water was removed via lyophilization. Methanol (80 mL) was then added to the water-insoluble portion and stirred at room temperature for 1 h. The soluble and insoluble portions were separated by filtration. The methanol-soluble portion was concentrated to ~10 mL using a rotary evaporator at ~25°C, poured into purified water (300 mL), and stirred at room temperature. The water-insoluble portion was recovered by filtration, and water was removed via lyophilization. *n*-Hexane (30 mL) was added to the water-insoluble portion and stirred at room temperature for 1 h. The resulting *n*-hexane-insoluble portion was recovered by filtration and dried under reduced pressure, yielding ECL–LPMS as a pale yellow powder (0.1043 g). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. 2b): δ 5.98–5.78 (br, 3H, –SiO(CH_3)(C*H*=CH_2)), δ 3.88–3.72 (br, 2H, –SiOC$H_2$$CH_3$), δ 3.68 (s, –SiO*H*), δ 1.23–1.16 (br, 3H, –SiOCH_2CH_3), δ 1.16–0.98 (br, 3H, –SiCHCH_3Si–), δ 0.98–0.83 (br, 1H –SiC*H*CH_3Si–), δ 0.76–0.30 (br, 4H –Si(CH_2)$_2$Si–), δ 0.26–−0.21. (br, 3H, –SiCH_3).^{29}Si NMR (79.4 MHz, $CDCl_3$, Fig. 3b): δ 9.91–6.60 (M), δ −7.11–−14.3 ($(D^2)_{c3}$) and (D^1), δ −18.1–−26.5 (D^2).

Preparation of ECL–LPMS–TMS (Scheme 1e). ECL–LPMS–TMS was prepared by reacting CTMS with the remaining silanol groups of ECL–LPMS for protection. Chloroform (2.0 mL) was added to ECL–LPMS (0.098 g, 0.670 mmol, based on the repeating unit (*n*) number). Separately, pyridine (0.620 g, 7.80 mmol) and CTMS (0.658 g, 5.94 mmol) were each dissolved in 2.0 mL of chloroform. The pyridine solution was added to the ECL–LPMS chloroform solution, followed by the CTMS solution, and the mixture was stirred at *ca*. 30°C for 50 min. The product was isolated by reprecipitating the chloroform from acetonitrile. The acetonitrile-insoluble portion was recovered via filtration, following which it was dried under reduced pressure, yielding ECL–LPMS–TMS as a white powder (0.066 g). GPC analysis revealed that the M_w and M_w/M_n values

of ECL–LPMS–TMS were 1.7×10^4 and 1.54, respectively (Fig. 1b). ^{1}H NMR (400 MHz, $CDCl_3$, Fig. 2c): δ 5.96–5.85 (br, 3H, –SiO(CH_3)(C*H*=CH_2)), δ 3.82–3.61 (br, 2H, –SiOCH_2CH_3), δ 1.28–1.12 (br, 3H, –SiOCH_2CH_3), δ 1.11–1.00 (br, 3H, –SiCHCH_3Si–), δ 0.95–0.76 (br, 1H – SiC*H*CH_3Si–), δ 0.76–0.34 (br, 4H –Si(CH_2)$_2$Si–), δ 0.29–−0.21. (br, 3H, – SiCH_3). ^{29}Si NMR (79.4 MHz, $CDCl_3$, Fig. 3c): δ 9.74–4.94 (M), δ −7.54–−11.3 ((D^2)$_{c3}$), δ −18.8–−27.3 (D^2).

Preparation of ECL–LPMS and ECL–LPMS–TMS cast films. ECL–LPMS cast films were prepared by dissolving 5 mg of ECL–LPMS in 0.1 mL of dehydrated DIBK, followed by stirring at room temperature for 15 min to ensure complete dissolution. The ECL–LPMS solution was then drop-cast onto a quartz glass substrate (12 × 20 mm) with the area adjusted using Teflon tape. The substrate was then heated on a hot plate at *ca*. 50°C for 1 h to remove the solvent, forming an ECL–LPMS cast film with a thickness of *ca*. 3–4 μm. ECL–LPMS–TMS cast films were prepared by dissolving 10 mg of ECL–LPMS–TMS in 0.2 mL of dehydrated DIBK, followed by stirring at room temperature for 15 min to ensure complete dissolution. The ECL–LPMS–TMS solution was drop-cast onto a quartz glass substrate (20 × 20 mm). The substrate was then heated on a hot plate at *ca*. 50°C for 1 h to remove the solvent, forming an ECL–LPMS–TMS cast film with a thickness of *ca*. 3–4 μm.

Preparation of aromatic polyimide cast films. Aromatic polyimide cast films were prepared by applying Pyre-M.L.® RC-5069 as a thin layer on a glass substrate (22 × 24 mm). The coated substrate was heated in an oven at 360°C for 3 h to form imide bonds through the dehydration of amic acid. Specific amounts of Pyre-M.L.® RC-5069 were weighed to prepare multiple films. From the prepared films, one with a thickness of ~10 μm was selected for analysis.

Preparation of the Sylgard 184 cast films. Sylgard 184 cast films were prepared according to a previously reported method.[36] First, 3.6 mL of the base-agent and 0.4 mL of the curing agent were weighed. The base agent and curing agent were mixed at a 10:1 ratio and dissolved in 96 mL of an *n*-hexane solution of Sylgard 184. Next, 0.5 mL of the Sylgard 184 solution was drop-cast onto a glass substrate (22 × 24 mm). The sample was then heated on a hot plate at 50°C for 1 h and then in an oven at 80°C for 12 h, forming a Sylgard 184 cast film with a thickness of *ca*. 5–7 μm.

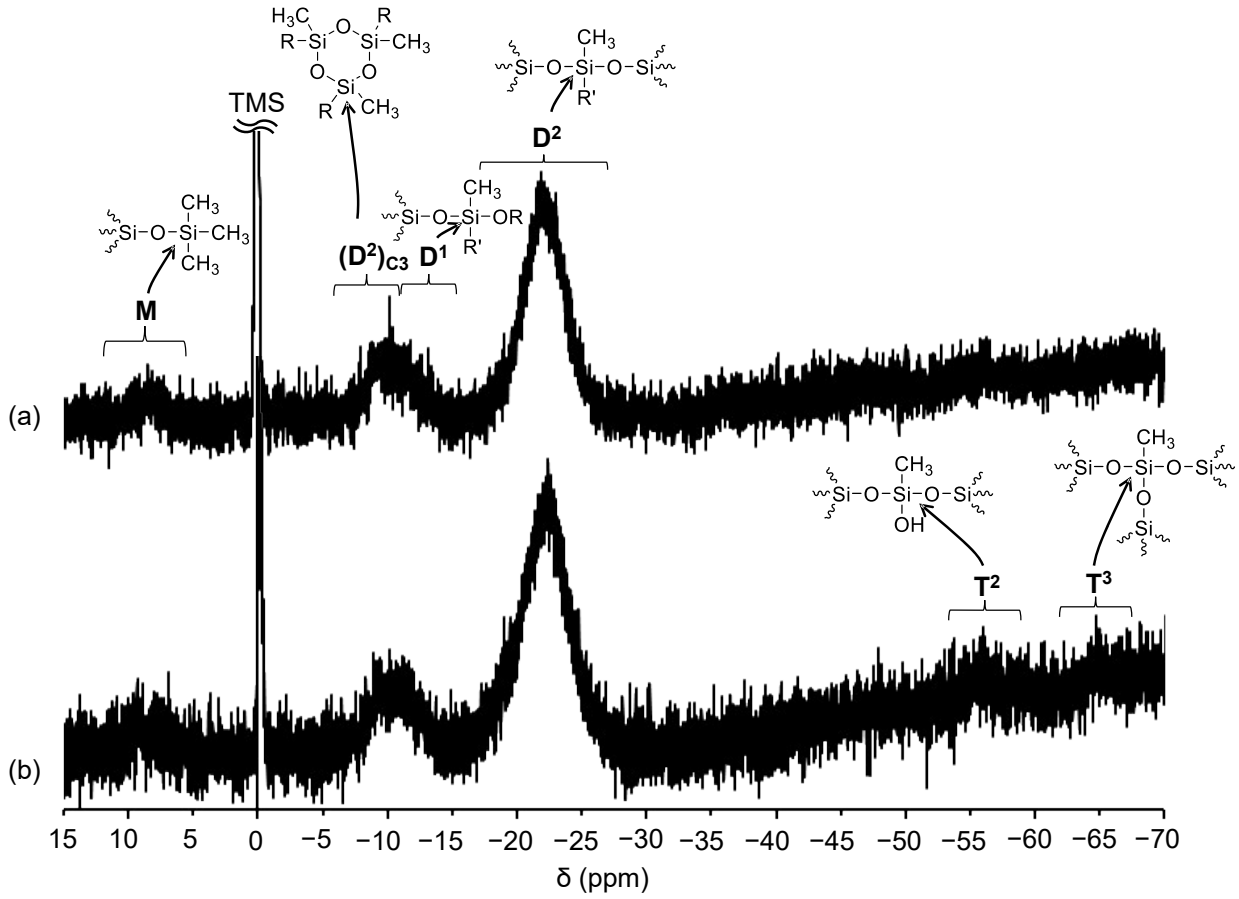

Fig. S1 ^{29}Si NMR spectra of (a) the original polymer (ECL–LPMS) and (b) the polymer prepared via template polymerization at a higher concentration (10 times the original) in $CDCl_3$. A small amount of $Cr(acac)_3$ was added as a relaxation agent. Chemical shifts are referenced to TMS (δ 0.0).

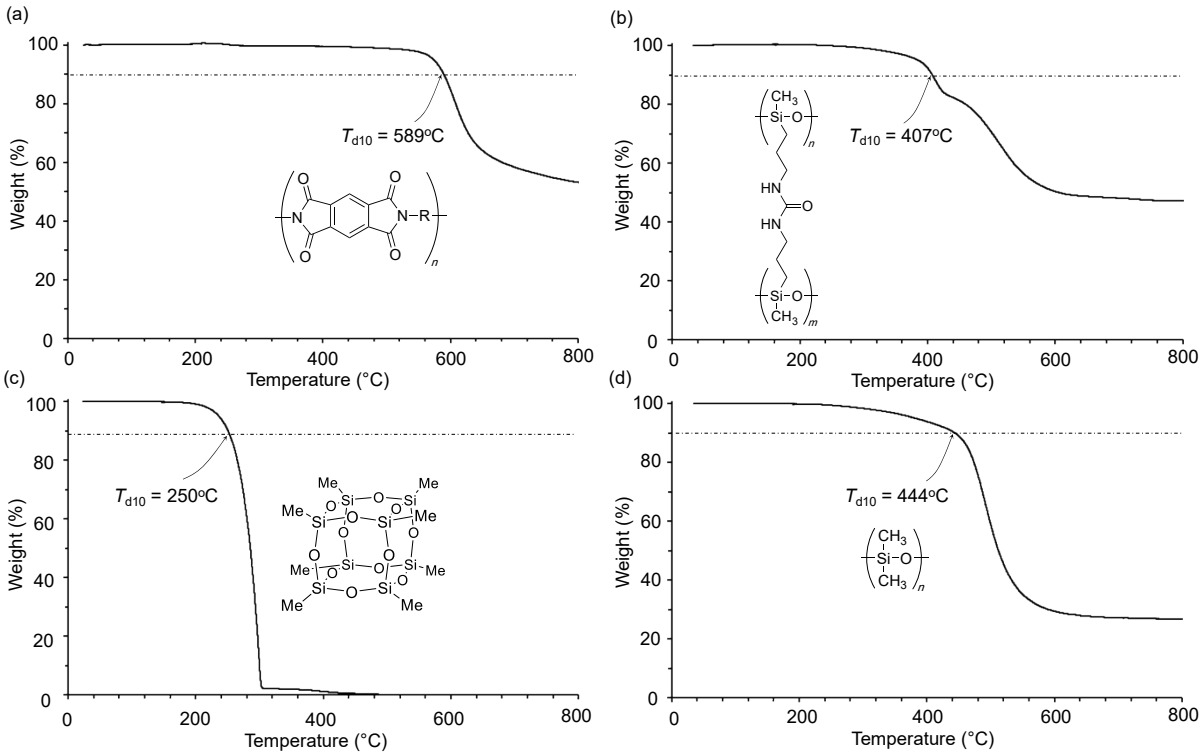

Fig. S2 TGA thermograms of (a) aromatic polyimide, (b) AUCL–LPMS, (c) Me–POSS and (d) Sylgard 184 under nitrogen flow at 100 mL min^{-1}.

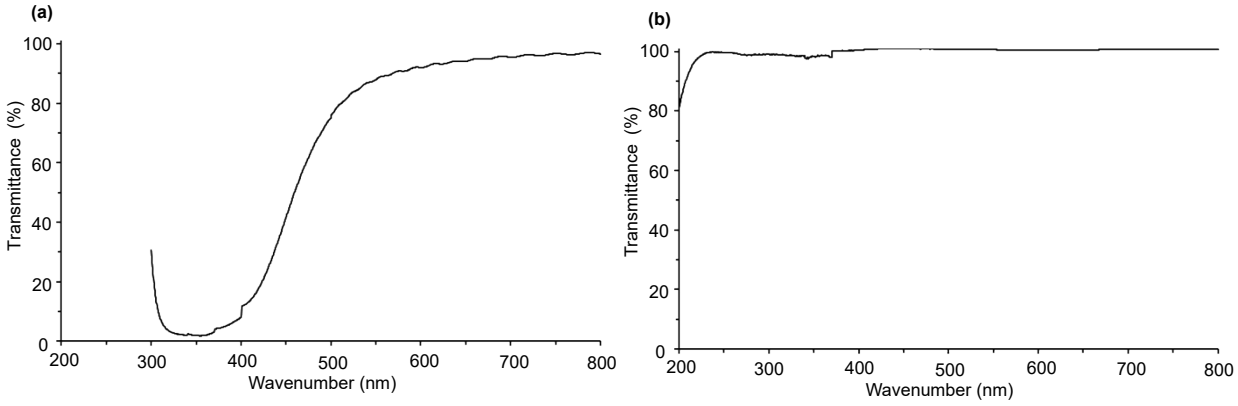

Fig. S3 Transmittance data of (a) aromatic polyimide and (b) Sylgard 184 cast films.