Electronically Supplementary Information for:

Synthesis of poly(methylsilsesquioxane-*co*-dimethylsiloxane) liquids and deep-ultraviolet transparent elastic resins through co-solvent-free water-rich hydrolytic polycondensation of organoalkoxysilanes

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Experimental procedure

Stock dilute hydrochloric acid with an H_2O : HCl molar ratio of 1 : 0.002 was prepared by diluting 5.703 g of 1.00 mol L^{-1} HCl (Fujifilm Wako Pure Chemical) with 44.515 g of distilled water. Methyltrimethoxysilane (MeTMS, Tokyo Chemical Industry) and dimethyldimethoxysilane (Me_2DMS, Tokyo Chemical Industry) were weighted (100 mmol in total) in a plastic container of 75 mL capacity and held at 20 °C by immersing the container in a water bath. A portion of the stock dilute hydrochloric acid was mixed with distilled water, and the resulting solution was added at once promptly to the mixture of MeTMS and Me_2DMS while stirring. The MeTMS : Me_2DMS : H_2O : HCl molar ratio of the mixture was f_T : 1 – f_T : x : 0.0002 with f_T = 0.8 or 0.9 and x = 3, 5, 10, 20, or 30. At f_T = 0.8, the amounts of MeTMS, Me_2DMS, and the stock dilute hydrochloric acid were 10.898, 2.404, and 0.181 g, respectively, and the amounts of distilled water were 5.224, 8.827, 17.835, 35.850, and 53.865 g at x = 3, 5, 10, 20, and 30, respectively. The plastic container containing the mixture was sealed and the mixture was stirred at 20 °C for 3 h. The resulting clear solution was aged without stirring at 80 °C in a conventional air-circulating oven for 1 day, during which the solution underwent liquid-liquid phase separation. Then, the container was cooled to room temperature and opened, the top layer of the biphasic solution was discarded by extraction, and the bottom layer was dried under vacuum at 60 °C for 1 day on a hot plate in a vacuum chamber (VOM-1000A, EYELA) evacuated by a rotary pump through a cold trap cooled with a refrigerator. The pressure at the exhaust port of the chamber was ~1 Pa in the late stage of the vacuum drying. The thermal curing of the vacuum-dried liquid samples was conducted in a heating chamber under a continuous N_2 flow. The liquid sample was transferred to a PTFE dish of 30 mm inner diameter and 12 mm height, and subjected to sequential heat treatment at 200 °C for 12 h and 250 °C for 24 h with a heating rate of 50 °C h^{-1} between the isothermal steps. This two-step heat treatment was necessary for the preparation of bubble-free monoliths.

A pH test paper (pH 1–11, 004, Johnson) was used to indicate the pH of liquid samples. Liquid-state ^{1}H and ^{29}Si nuclear magnetic resonance (NMR, JNM-ECS300, JEOL) spectra were recorded in a single pulse sequence with pulse flip angles of 45 and 30°, respectively, and relaxation delays of 5 and 20 s, respectively. Viscosity measurements (EMS-1000S, KEM) were performed at 40 °C to lower the viscosity of samples as the upper measurement limit of the viscometer was ~10^6 mPa s. Viscosity did not change during the measurement at 40 °C. Gel permeation chromatography (GPC, column: KF-804L Shodex, detector: RID-10A Shimadzu) was conducted using tetrahydrofuran as the eluent at a flow rate of 1.0 mL min^{-1}. Differential scanning calorimetry (DSC, X-DSC7000, Hitachi) was performed at a heating rate of 5 °C min^{-1} in a sealed aluminum pan containing ~14 mg of sample.

The mechanical properties of thermosetting resins were characterized by pencil hardness tests, uniaxial load-unload tests (Micro Autograph MST-I, Shimadzu), and Vickers microindentation tests. The Vickers microindentation tests were performed with a homemade indenter with an inverted optical microscope (GX53, Olympus) equipped with a 50× objective lens (LCPLFLN50XLCD, Olympus) and a CCD camera.[1] Optical absorption spectra were measured using a conventional spectrometer (U-4100, Hitachi). Refractive index and Abbe number were evaluated using an Abbe refractometer (DR-M4, Atago) using glycerol as a contact liquid. Density was measured using a pycnometer with water as the reference liquid. Simultaneous thermogravimetric and differential thermal analysis (TG-DTA, STA7300, Hitachi) was conducted at a heating rate of 5 °C min^{-1} in air in a platinum pan containing ~8 mg of powdered sample.

Reference

1. S. Yoshida, M. Kato, A. Yokota, S. Sasaki, A. Yamada, J. Matsuoka, N. Soga and C. R. Kurkjian, *J. Mater. Res.*, 2015, **30**, 2291–2299.

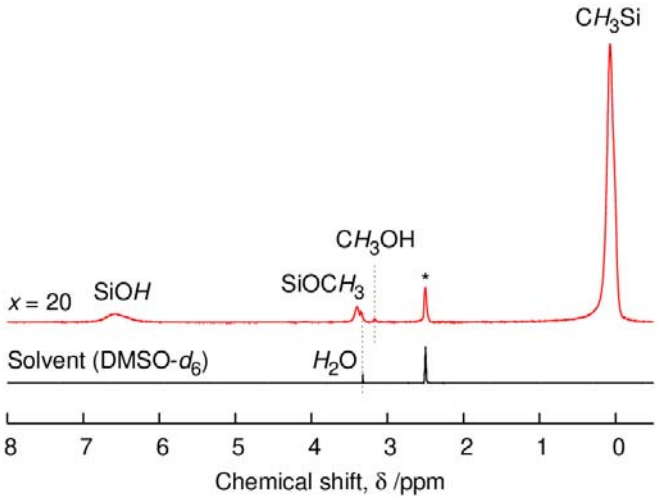

Fig. S1 ^{1}H NMR spectrum of a poly(MeT-*co*-Me$_2$D) liquid prepared at (f_T, x) = (0.8, 20) (300 MHz, DMSO-d_6). Spectrum of pristine DMSO-d_6 solvent is also shown to indicate the amount of impurity water in the solvent. The asterisk at ~2.5 ppm indicates the solvent residual peak. The residual water to Si molar ratio, calculated from the equation $I_{H2O}/2 \times (r_{sample} - r_{DMSO})/r_{sample} \times (3\times0.8 + 6\times0.2)/I_{CH3Si}$, where I_{H2O} (~1.12×10^{-4}) and I_{CH3Si} (3.6) are the intensities of the H_2O and CH_3Si peaks in the sample, respectively, and r_{sample} (~0.0744) and r_{DMSO} (~0.0558) are H_2O to solvent residual peak intensity ratios in the sample and DMSO-d_6, respectively, was ~0.0014.

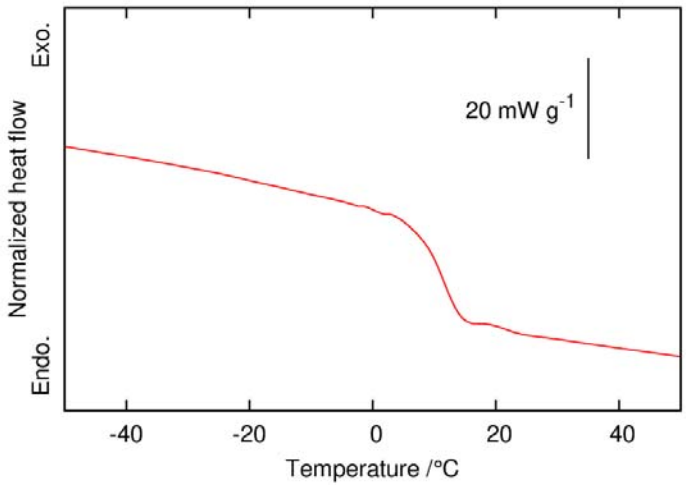

Fig. S2 DSC curve of a poly(MeT-*co*-Me$_2$D) liquid prepared at (f_T, x) = (0.8, 20).

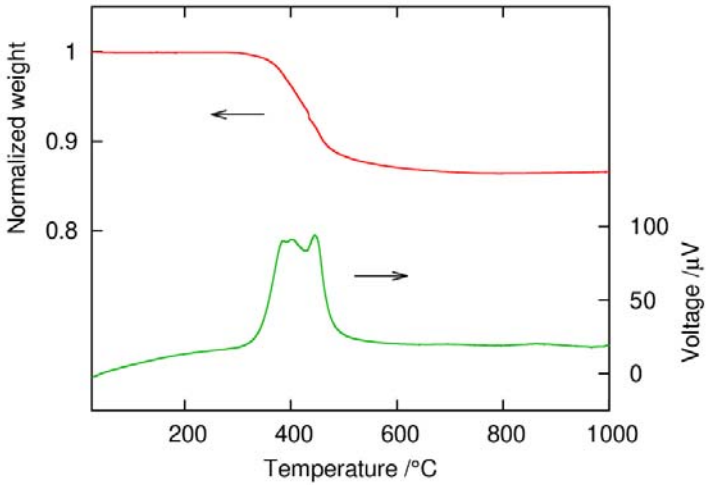

Fig. S3 TG-DTA curves of a poly(MeT-*co*-Me_2D) resin prepared at (f_T, x) = (0.8, 20) and subjected to sequential heat treatment at 200 °C for 12 h and 250 °C for 24 h.