

Supporting Information for
**Molecular Understanding for Large Deformations of Soft Bottlebrush
Elastomers**

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Materials and Methods

Materials. All chemicals are purchased from Sigma-Aldrich (St. Louis, MO) unless otherwise noted. All reactive polydimethylsiloxane (PDMS) polymers are purchased from Gelest[®] Inc. (Philadelphia, PA). Backbone: vinylmethylsiloxane–dimethylsiloxane copolymer, trimethylsiloxy terminated, 300 vinyl groups per molecule, molecular weight (MW) 50,000 g/mol (VDT-5035). Side chain: mono-hydride terminated polydimethylsiloxane, MW 4,750 g/mol (MCR-H21). Crosslinking chain: hydride-terminated polydimethylsiloxane, MW 17,200 g/mol (DMS-H25).

Gel permeation chromatography (GPC). The polymers are passed through aluminum base column to remove inhibitors before use. The polymers are characterized using GPC (TOSOH EcoSEC HLC-8320), which is equipped with two TOSOH Bioscience TSKgel GMH_{HR}-M 5 μ m columns in series and a refractive index detector at 40 °C. High-performance liquid chromatography (HPLC) grade tetrahydrofuran (THF) is used as the eluent with a flow rate of 1mL/min. The samples are dissolved in THF with a concentration around 3 mg/mL.

The polydispersity index (PDI) values of the side chain, backbone, and crosslinking chain are 1.15, 2.54, and 1.64, respectively, as shown by the GPC profiles in **Fig. S1a**. During GPC characterization, polymers are separated based on the difference in sizes. For linear polystyrene (PS) and linear PDMS of the same molecular weight, however, their sizes are not the same because of their difference in chemical structure and solubility in THF; this would result in different dependence of MW on elution time. Therefore, instead of using PS polymers as standards, we use custom-synthesized linear PDMS with known molecular weights to obtain the calibration curve. The molecular weights of the three linear PDMS polymers are confirmed to agree with the provided values, as shown in **Fig. S1b**.

Bulk rheology

The PDMS linear polymers are mixed at a predetermined mass ratio to achieve different densities of crosslinking chains. Catalyst, 2% platinum in xylene, the so-called Karstedt's catalyst, is added at the concentration of 5 ml/g. The mixture is cured at 80°C for 40 hours to reach a steady shear storage modulus. Rheological experiments are carried out on a stress-controlled rheometer (MCR302, Anton Paar) with 50 mm plate-plate geometry at a gap of 750 μ m. After complete crosslinking, the temperature is lowered to 20°C, which causes the shrinkage of the PDMS volume and thus gap contraction. The change in normal force due to the gap contraction with temperature is alleviated by adjusting the gap height. In our measurements, the normal force is kept at 0.05-0.1 N, equivalent to the normal stress of 25-50 Pa; this ensures a good contact between the geometry and the sample yet that the compressive strain is <1%, within the linear elastic deformation of the soft PDMS elastomers.

In our measurements, we tune the shear moduli by controlling the density of crosslinking chains, as described in ref. (1).

Tensile tests

We perform tensile tests for bottlebrush elastomers using Instron[®] 3342 with a 10N load cell. A dumbbell-shaped sample has a central part of 16mm in length, 6mm in width, and about 4mm in thickness. Cyclic uniaxial tensile measurements are conducted at room temperature in the air using different strain rates, including 1.67×10^{-3} , 1.67×10^{-2} , and 1.67×10^{-1} /sec (**Fig. S2**). Cyclic extension tests with incremental elongation are performed on the same tensile machine at a strain rate of 1.04×10^{-3} /sec. The maximum strains of the cyclic extension tests include 0.13, 0.26, and until the sample fractures.

To prepare the samples for tensile tests, we use a custom-machined Teflon mold to make dumbbell-shaped bottlebrush elastomers by curing precursor polymers *in situ*. The elastomers are elastic and fragile, and can be easily damaged when being clamped by tensile grips. To this end, for each of the two ends of a dumbbell-

shaped sample, we glue both the front and back sides with a hard paper board, which has a low flexural strength but of a high tensile modulus on the order of GPa. The hard paper boards are used as handles for the tensile grips. This prevents direct mechanical compression from the tensile grips to the bottlebrush elastomers, ensuring minimal sample damage during tensile tests.

Although the above procedure, in principle, should allow us to obtain reliable, repeatable measurements, it remains difficult to avoid sample damage when isolating the dumbbell-shaped samples from the Teflon mold. Therefore, we use large amplitude oscillatory shear measurements as the major means to quantify the extensibility of the elastic, non-dissipative bottlebrush elastomers.

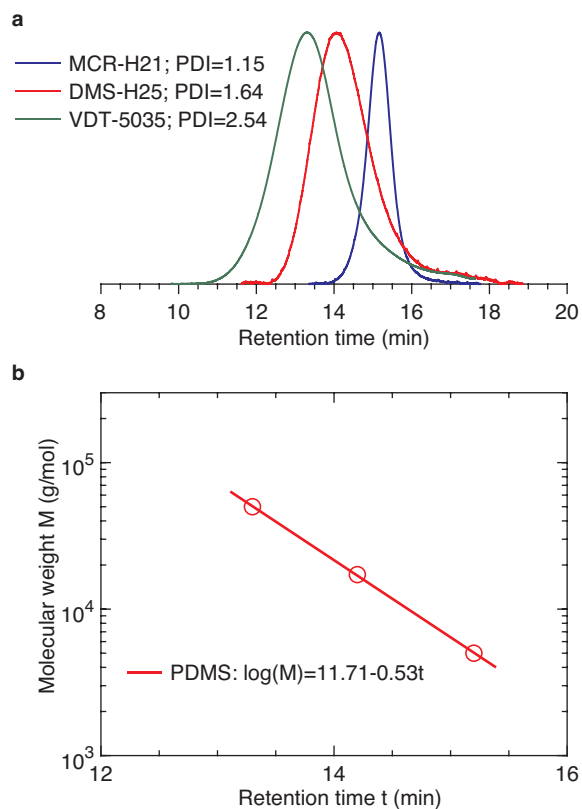


Figure S1. Polydispersity index (PDI) and molecular weight of linear PDMS polymers. (a) GPC characterization of three linear PDMS polymers: MCR-H21, side chain with the PDI of 1.15; DMS-H25, crosslinking chain with the PDI of 1.64; VDT-5035, backbone with the PDI of 2.54. **(b)** Dependence of molecular weight, M , on the retention time, t , for linear PDMS polymers in **(a)**. Solid line: the calibration curve for PDMS.

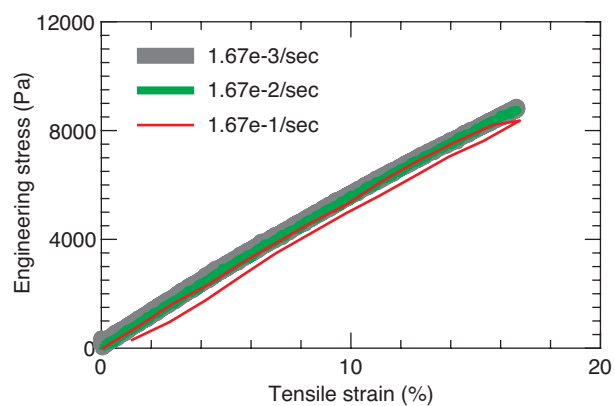


Figure S2. Bottlebrush elastomers are elastic, non-dissipative. Cyclic tensile tests show that at various strain rates the loading and unloading stress-strain curves are nearly perfectly overlapping with each other, suggesting that the bottlebrush elastomers are elastic, non-dissipative.

References

- 1 L.-H. Cai, T. E. Kodger, R. E. Guerra, A. F. Pegoraro, M. Rubinstein and D. A. Weitz, *Adv. Mater.*, 2015, **27**, 5132–5140.