Supporting Information

Adhesion and Mechanical Properties of Poly(dimethyl siloxane) Bottlebrush Elastomers

Hyemin Kim, James J. Watkins*, and Alfred J. Crosby*

Department of Polymer Science and Engineering, University of Massachusetts Amherst,

Amherst, Massachusetts 01003, United States

* Corresponding Authors Email: watkins@polysci.umass.edu (J.J. Watkins) and crosby@mail.pse.umass.edu (A.J. Crosby)

Table S1. Macromonomers used for free radical polymerization

Macromonomer	M_n for ^{1}H NMR[a]	Polydispersity from GPC[b]
MCR-M11	982 g/mol	1.1
DMS-R18	4530 g/mol	1.1

a. In CDCl$_3$ at 25 ˚C (500 MHz)

b. In THF at 25 ˚C

Figure S1. ^{1}H NMR

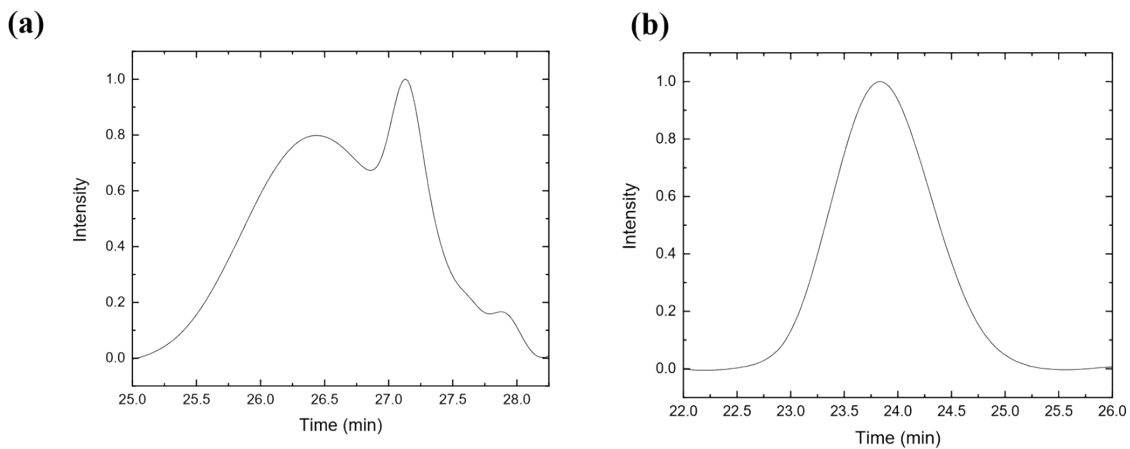**Figure S2**. ^{1}H NMR spectrum of DMS-R18 in CDCl$_3$

(a)

(b)

Figure S3. THF GPC of **(a)** MCR-M11 and **(b)** DMS-R18. The right half of (a) is distorted because it occurs outside the limits of detection.
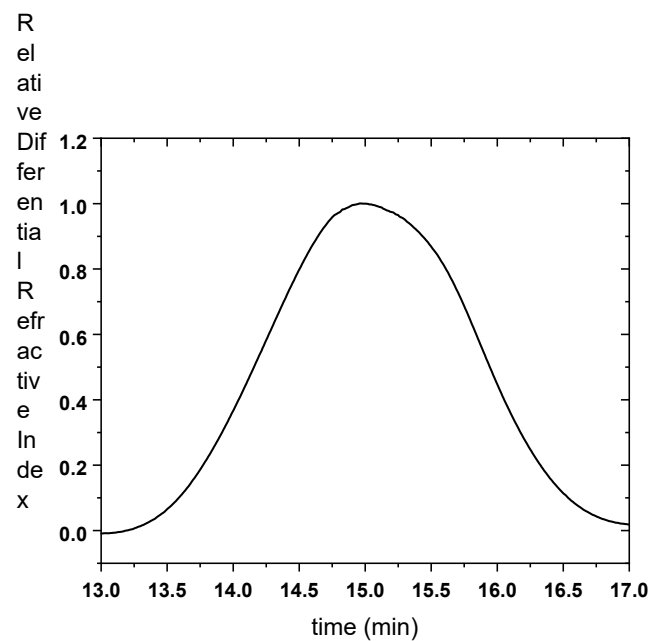

Figure S4. GPC multiangle laser light scattering (MALLS) curve of the uncrosslinked PDMS bottlebrush polymer in THF

4

Table S2. Architectural parameters for poly (methylmethacrylate) (PMMA), poly (dimethylsiloxane) (PDMS)

Architectural parameter	PMMA	PDMS
Monomer length[1]	0.25 nm	0.31 nm
Kuhn length[1]	1.50 nm	1.30 nm
Monomer volume[2]	0.15 nm^3	0.13 nm^3

Table S3. Gel fractions[a] of BBEs and linear chain networks

BBEs	Gel fractions	Linear chain networks	Gel fractions
nx=17	88.3±1.2 %	Syl 40	85.6±0.5 %
nx=25	86.6±0.4 %	Syl 50	83.4±0.2 %
nx=34	86.2±0.4 %	Syl 55	84.3±0.9 %

a. Gel fractions were determined from more than five samples prepared over multiple dates to confirm repeatability of sample preparations.
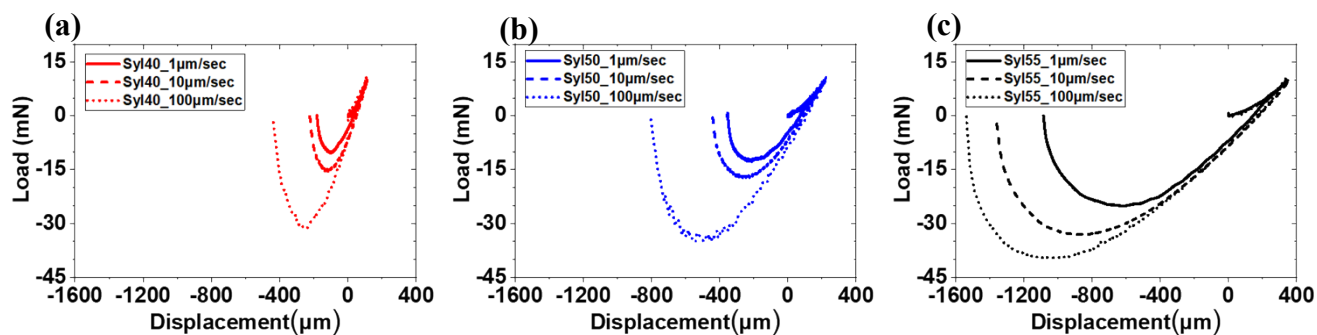
Figure S5. Load-displacement curves of linear chain networks with different displacement rates (1, 10, and 100 μm/sec)
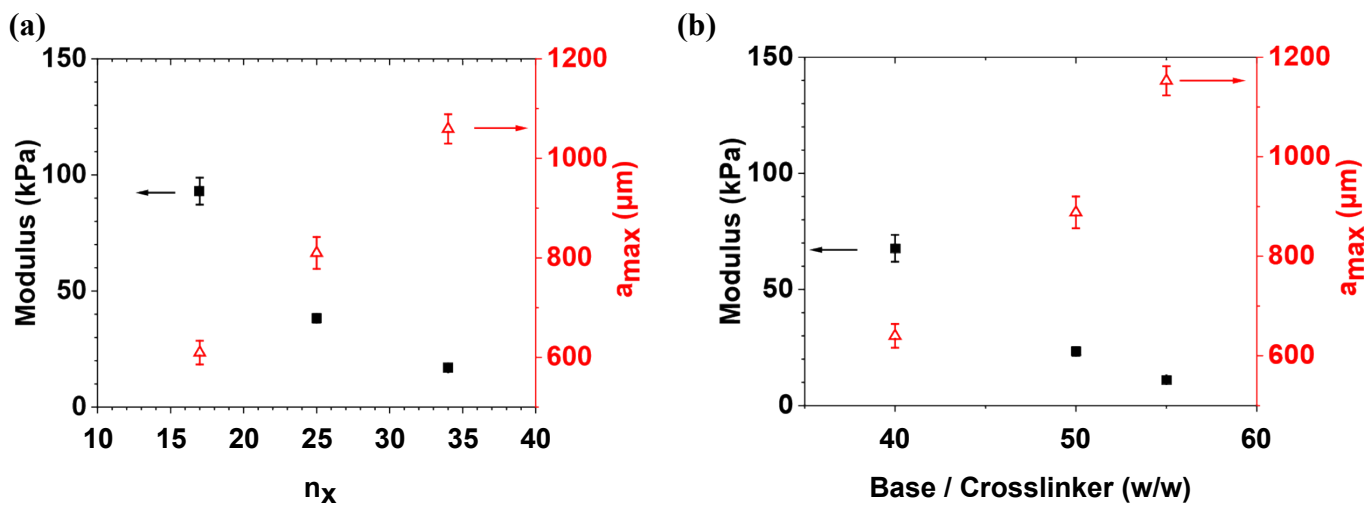

Figure S6. Elastic moduli and maximum contact radii of **(a)** BBEs and **(b)** linear chain networks from CAT measurements with a displacement rate of 10μm/sec

- **Calculation of energy release rate, GG_{cc}**

$$GG_{cc} = -\frac{(PP'-PP)^2 \, dddd}{4\pi\pi\pi\pi \, dd\pi\pi} \qquad \textbf{(Eq S1)}$$

where PP' is the force in the absence of adhesion, PP is the force, aa is the contact radius, and CC is the compliance. To account for the confined geometry, PP', $\delta\delta'$ (displacement in the absence of adhesion), and CC have correction factors.[3]

$$PP' = 3 \qquad RR4(EE1-\pi\pi3vv2) \; 1 + 0.33(\pi\pi h)3 \qquad \textbf{(Eq S2)}$$

$$\delta' = \pi\pi^2 \, 0.4 + 0.6\exp -1.8 \, \pi\pi \qquad \textbf{(Eq S3)}$$
$$RR \qquad\qquad h$$

$$CC = \frac{(1-vv^2)}{} \; 1 + \frac{4\,\pi\pi}{} + \frac{4\,\pi\pi}{}^{3} -1 \qquad \textbf{(Eq S4)} \; 2EE\pi\pi \; 3\,h \; 3\,h$$

where RR is the radius of a probe, h is the thickness of the elastomer, and vv is the Poisson's ratio.

CC is determined from the slope of displacement versus force.

$$CC = \frac{\delta\delta'-\delta\delta}{PP'-PP} \qquad \textbf{(Eq S5)}$$

Table S4. E, GG_{00} and vv^* of BBEs from CAT measurements.

BBEs	E (kPa)[a]	GG_{00} (J/m^2)	vv^* (μm/sec)
n = 17 x	93.0±5.8	0.179±0.024	77.74±12.17
n = 25 x	38.3±1.9	0.177±0.032	32.55±4.03
n = 34 x	16.9±0.5	0.185±0.020	27.13±3.11

a. E were determined when the displacement rate is 10 μm/sec.

Table S5. E, GG_{00} and vv^* of linear chain networks from CAT measurements

Linear networks	E (kPa)[a]	GG_{00} (J/m^2)	vv^* (μm/sec)
Syl 40	67.7±5.3	0.484±0.037	4.11±0.40
Syl 50	23.2±3.5	0.808±0.236	3.65±0.35
Syl 55	11.1±1.6	1.305±0.301	2.01±0.19

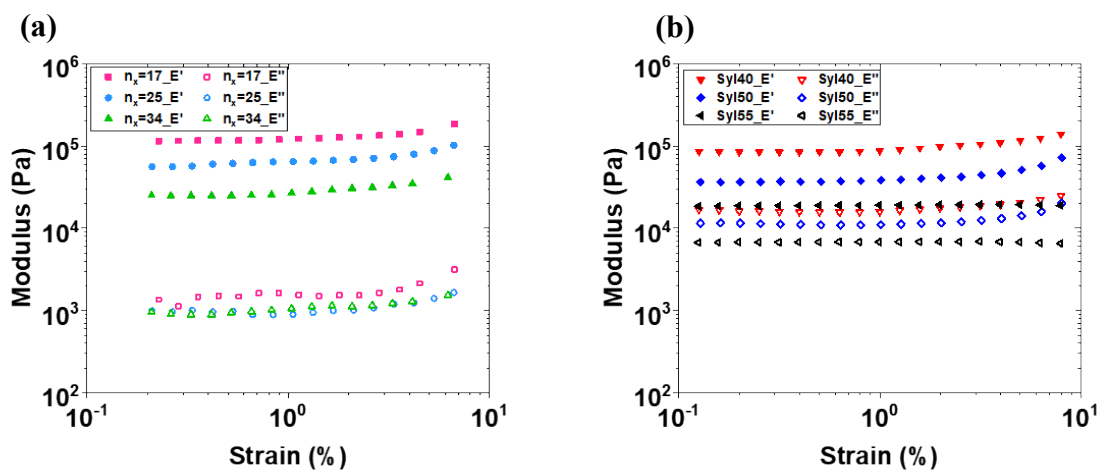a. E were determined when the displacement rate is 10 μm/sec.

Figure S7. Strain dependence of viscoelastic properties of **(a)** BBEs and **(b)** linear elastomers at the frequency = 1Hz by DMA at room temperature. Solid data points are elastic storage moduli (**E′**) and open data points are loss moduli (**E″**).
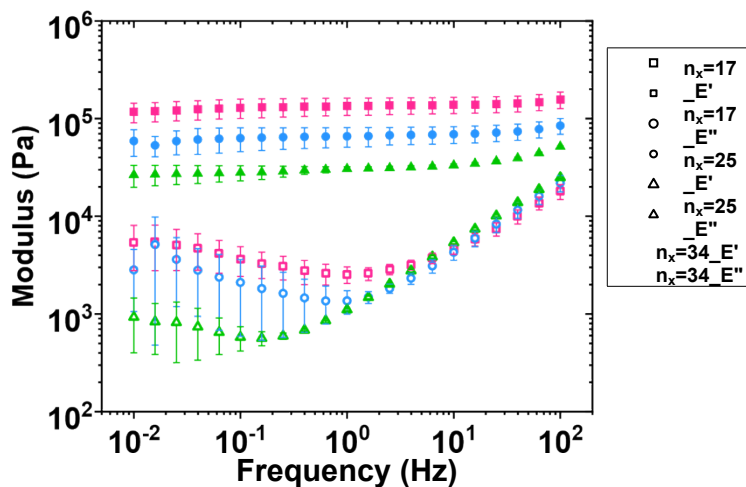

Figure S8. Frequency dependence of viscoelastic properties of BBEs at the strain = 1% by DMA at room temperature. Solid data points are elastic storage moduli (**E′**) and open data points are loss moduli (**E″**).
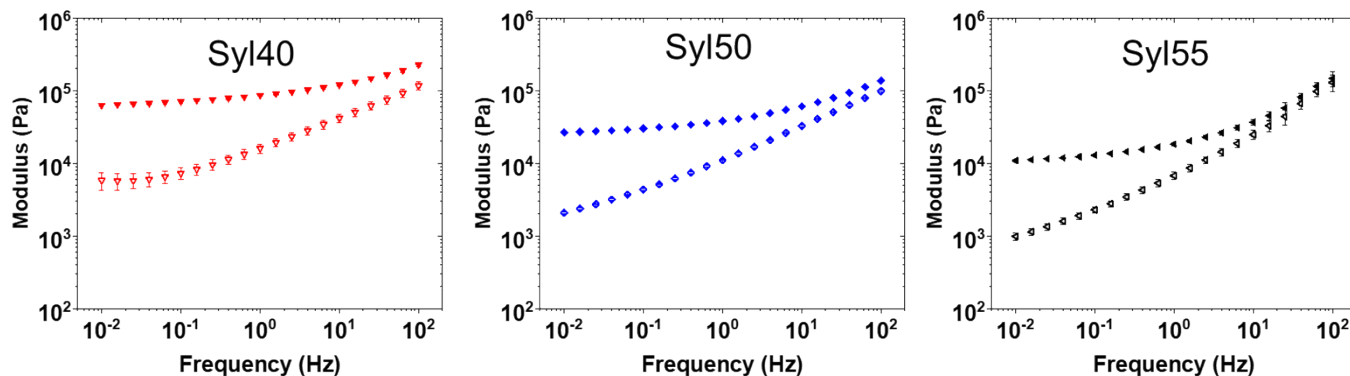
Figure S9. Frequency dependence of viscoelastic properties of linear chain networks at the strain = 1% by DMA at room temperature. Solid data points are elastic storage moduli (E') and open data points are loss moduli (E'').
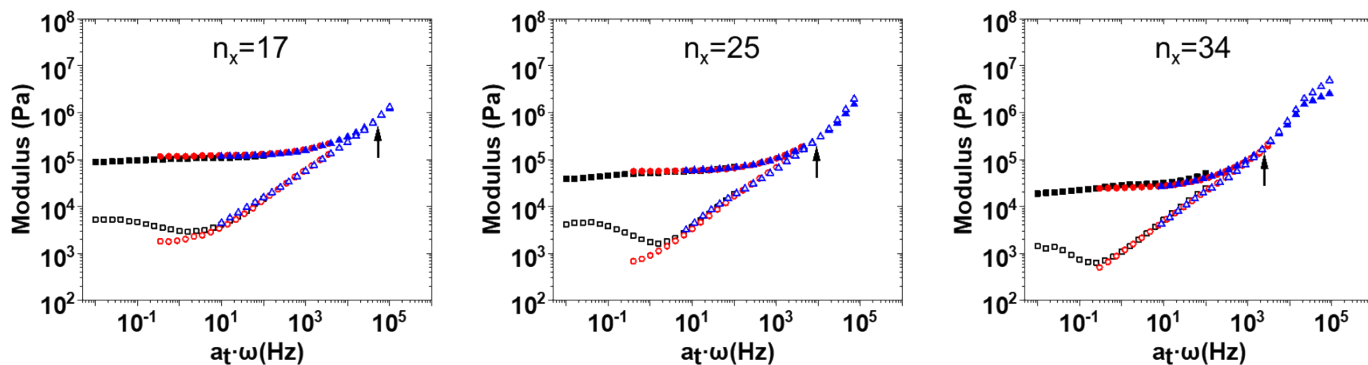

Figure S10. Time temperature superposition plots of BBEs at the strain = 1% by DMA at ■ = 22 °C, ● = -50 °C, and ▲ = -75 °C. Solid data points are elastic storage moduli (E'), open data points are loss moduli (E''). An arrow is the crossing point, ω_{BBBB}, of E' and E''.

Table S6. Network relaxation time, τ_{BBBB}, of BBEs. τ_{BBBB} were determined as the inverse of

the frequency at the crossing point, ω_{BBBB}, from **Figure S9**.

BBEs	ω_{BBBB} (Hz)	τ_{BBBB} (sec)
$n = 17_x$	5.50±0.62 E+4	1.83±0.20 E-5
$n = 25_x$	9.00±1.01 E+3	1.12±0.13 E-4
$n = 34_x$	2.40±0.20 E+3	4.19±0.35 E-4

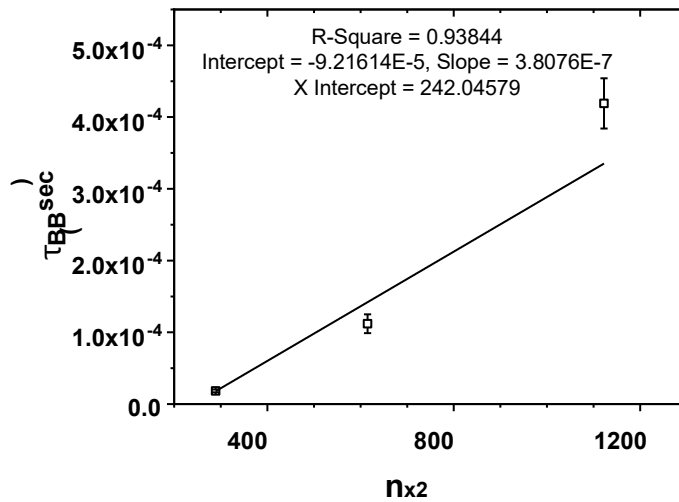**Figure S11**. A plot of τ_{BBBB} and n_x^2 of BBEs. The equation of fitting is $\tau_{BBBB} = \tau_0 (n_{sc} + 1)^{3/2} n_x^2$ where n_{sc} is 14 and τ_0 is the monomer relaxation time.[4]

Table S7. Characteristic relaxation time, τ_{llllll} , of linear chain networks. τ_{llllll} were determined as the inverse of the frequency at the crossing point, ω_{llllll}, obtained by extrapolation

from **Figure S8**. Linear fitting lines for **E′** and **E″** fit well over 1 – 100 Hz with R squared = 0.98 – 0.99 in log-log plots (**Figure S8**). Possible highest and lowest of **E′** and **E″** were calculated by adding or subtracting the standard deviation from the average.

Linear networks	ω_{max} (Hz)	τ_{min} (sec)
Syl 40	4.89±3.25 E+3	2.66±1.46 E-4
Syl 50	1.02±0.15 E+3	9.96±1.39 E-4
Syl 55	4.25±5.03 E+2	8.22±9.69 E-3

References

1. M. Vatankhah-Varnosfaderani, W. F. Daniel, M. H. Everhart, A. A. Pandya, H. Liang, K. Matyjaszewski, A. V. Dobrynin and S. S. Sheiko, Nature, 2017, **549**, 497-501.

2. J. E. Mark, Physical properties of polymers handbook, Springer, 2007.

3. K. R. Shull, D. Ahn, W. L. Chen, C. M. Flanigan and A. J. Crosby, Macromolecular Chemistry and Physics, 1998, **199**, 489-511.

4. Z. Cao, W. F. Daniel, M. Vatankhah-Varnosfaderani, S. S. Sheiko and A. V. Dobrynin, Macromolecules, 2016, **49**, 8009-8017.