Thermomechanical properties and glass dynamics of polymer tethered colloidal particles and films

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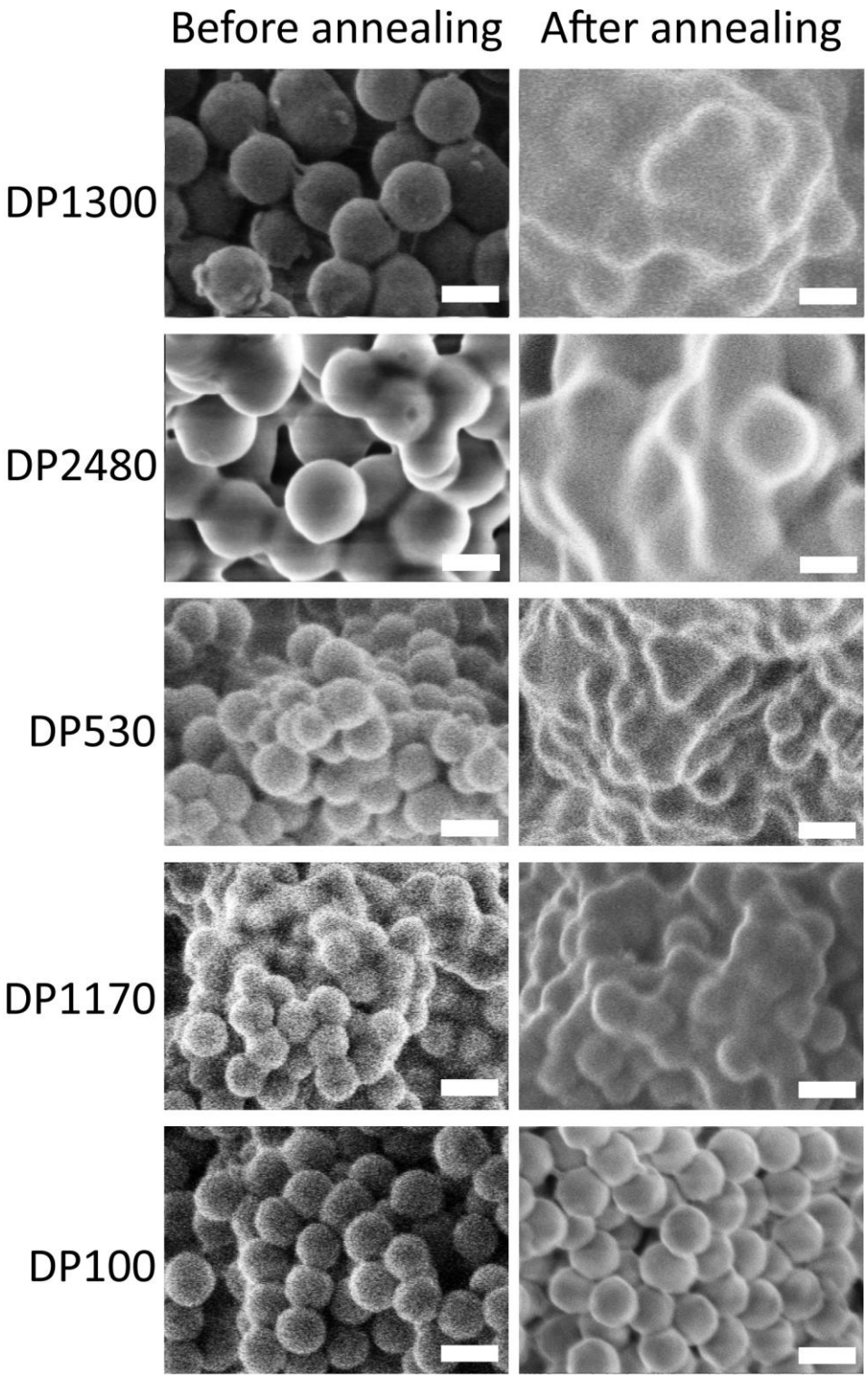

Figure S1. SEM images (Scale bar: 200 nm) of particle brushes measured before and after annealing process.

The key parameter ϕ_{PS} of samples is determined independently by five different methodologies shown as following.

1. By calculating the brush volume from the grafting density, the density of bulk PS (1050 kg/m^3), the interparticle distance (d) and radius of silica (R), where d and R were obtained from the TEM images:

$$V_{PS} = \frac{4\pi R^2 \sigma M n}{\rho_{PS} V_A},\ V_{SiO2} = \frac{4\pi R^3}{3},\ V_{Brush} = \frac{4\pi(\frac{d}{2})^3}{3}$$

$$\Phi_{PS-1} = \frac{V_{PS}}{V_{PS}+V_{SiO2}},\quad \Phi_{PS-2} = \frac{V_{PS}}{V_{Brush}}$$

2. Calculation based on the assumption of a FCC assembly structure, where diameter of particle brush (d) and radius of silica (R) are determined from TEM images:

$$\Phi_{ps-3} = 1 - V_{silica} = 1 - \frac{4\sqrt{2}\pi R^3}{3d^3}$$

3. From the individual particle brushes, using the dimension of singe particle brush (d) as obtained from the SEM images and radius of silica (R) obtained from TEM images:

$$\Phi_{PS-4} = 1 - \frac{(2R)^3}{d^3}$$

4. From thermogravimetric analysis of brush particle solids that yields the volume fraction of inorganic component from the amount of solid that is retained after pyrolysis of the materials. The organic (PS) weight fraction can be calculated subsequently as follows:

$$\Phi_{PS-5} = 1 - \frac{\Phi_{SiO_2,wt} \cdot \rho_{PS}}{\left(1 - \Phi_{SiO_2,wt}\right) \cdot \rho_{SiO_2} + \Phi_{SiO_2,wt} \cdot \rho_{PS}}$$

Table S1. Volume fraction of polystyrene is determined by different methods

	Φ_{PS-1}	Φ_{PS-2}	Φ_{PS-3}	Φ_{PS-4}	Φ_{PS-5}	$\Phi_{average-PS}$
DP1300	0.85	0.67	0.91	0.87	0.82	0.86±0.04
DP2480	0.89	0.63	0.94	0.93	0.90	0.93±0.03
DP530	0.54	0.45	0.72	0.54	0.56	0.56±0.02
DP1170	0.44	0.52	0.50	0.49	0.47	0.50±0.02
DP100	0.41	0.36	0.62	0.72	0.41	0.48±0.04

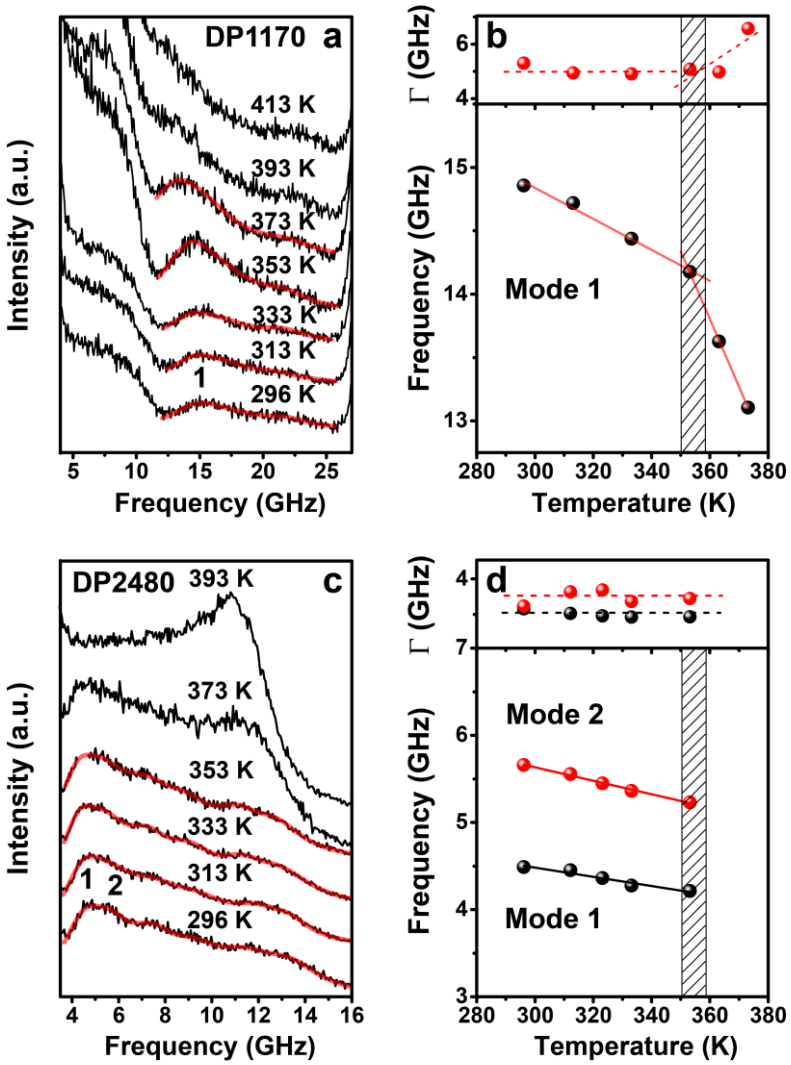

Figure S2. Evolution of eigenmode spectra of DP1170 (a) and DP2480 (c) with increasing temperature. The peak frequency (low panel) and linewidth (upper panel) of the strongest modes for DP1170 (b) and DP2480 (d) are plotted as a function of temperature. The vertical shaded area in (b,d) indicates the glass transition region in DP1170.

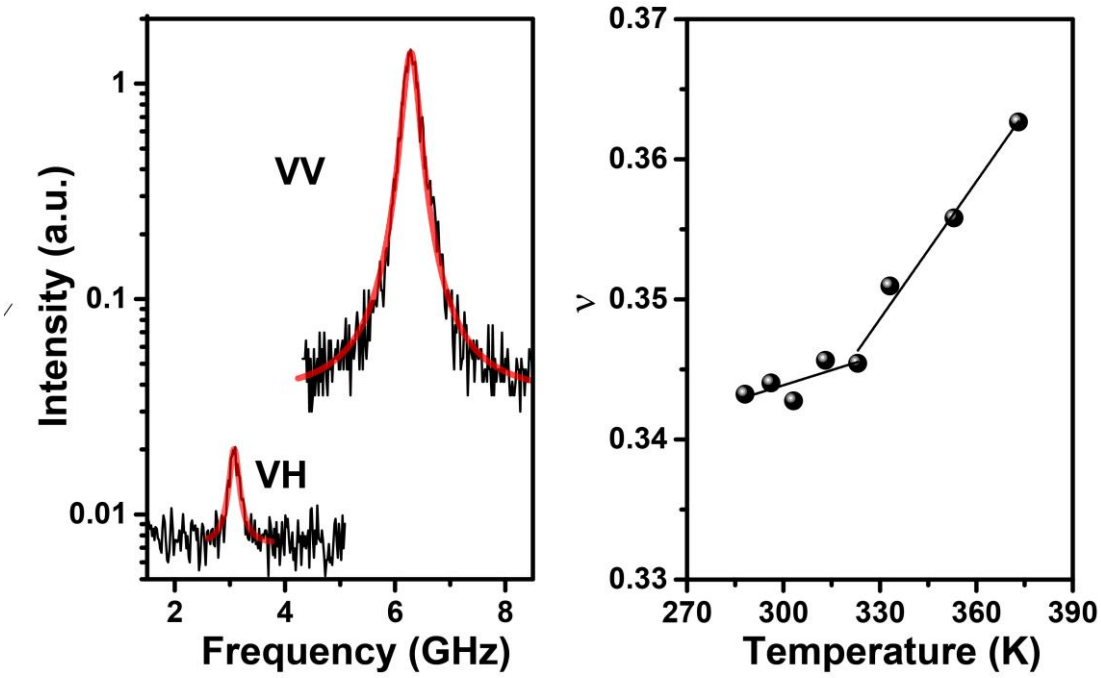

Figure S3. (a) Polarized (VV) and depolarized (VH) BLS spectra of PS2k (Molecular weight 2000 g/mol) at 295K. (b) The variation of Poisson's ratio with temperature. (The Poisson's ratio: $\nu = \frac{C_L^2 - 2C_T^2}{2(C_L^2 - C_T^2)}$)

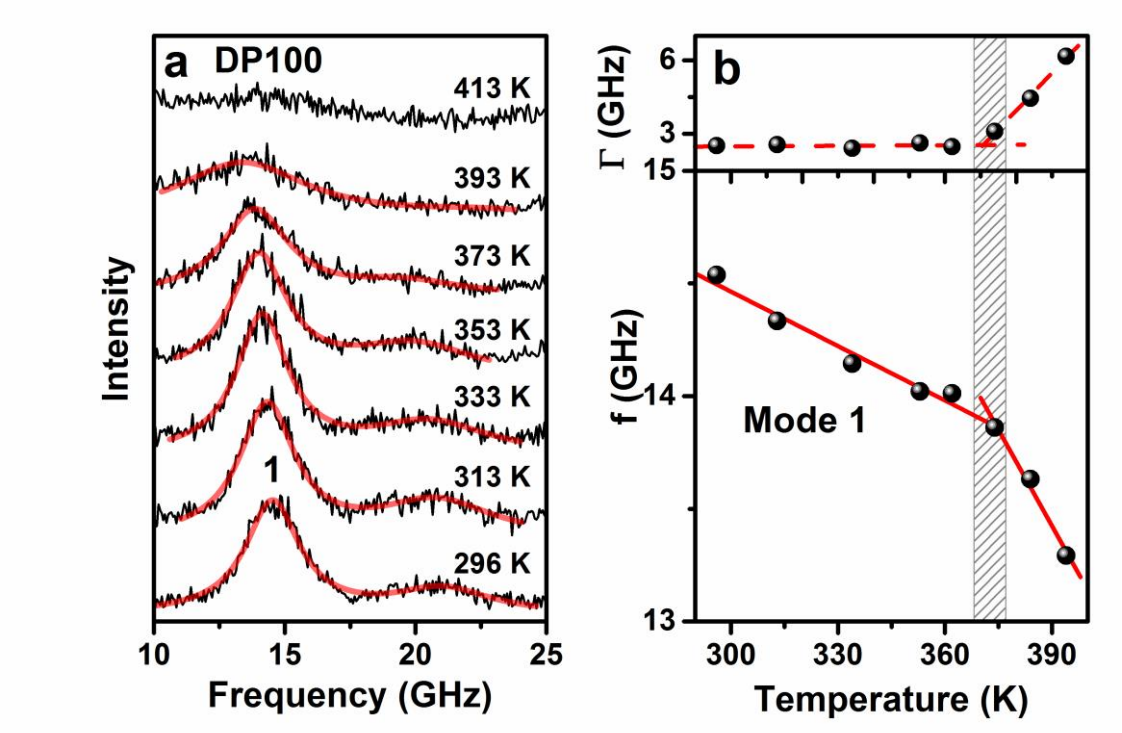

Figure S4. (a) Evolution of eigenmode spectra of DP100 with increasing temperature. (b) Temperature dependence of the peak frequency (low panel) and linewidth (upper panel) of the strongest mode in the DP100 spectra. The vertical shaded area indicates the glass transition region.

Table S2. Summary of T_g of particle brush systems as determined by DSC.

T_g/K	DP1300	DP2480	DP530	DP1170
1st Run	343 352 373	358 379	354 381	349 382
2nd Run	353	382	353 381	382
3rd Run	356	382	362 382	382

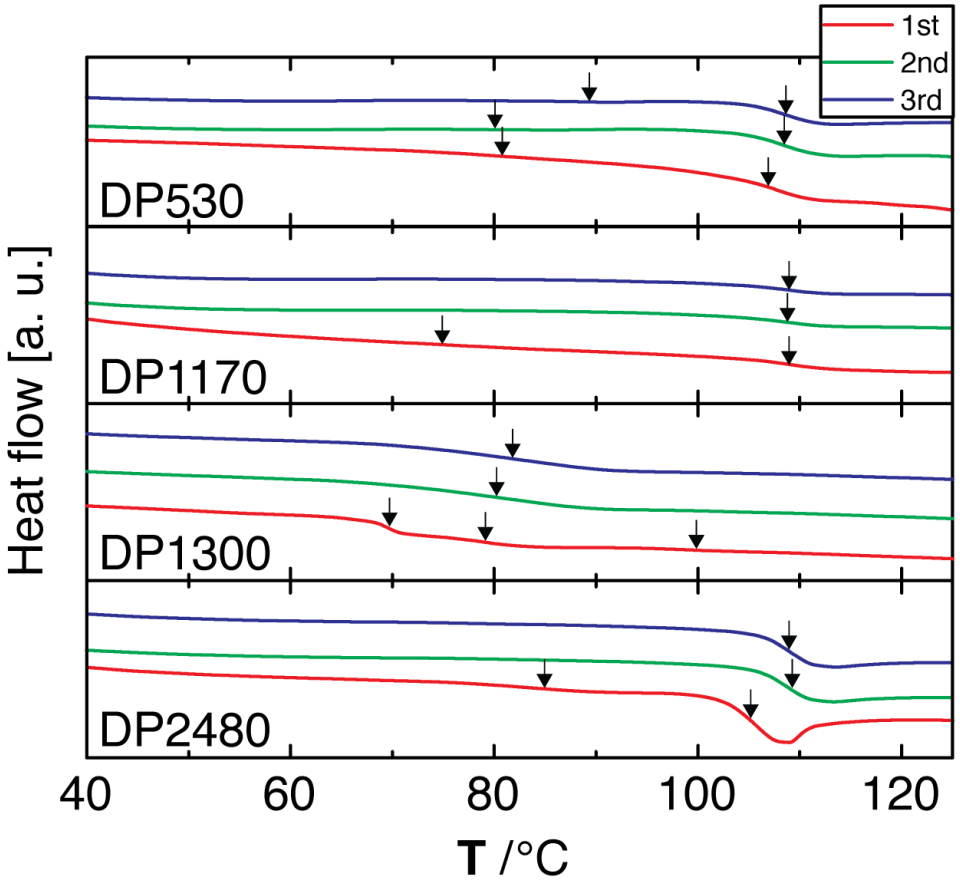

Figure S5. DSC traces of particle brush systems recorded during heating (cooling) of materials at a rate of 10 K /min (20 K / min, see text for more details) representing the 1st run (red), 2nd run (green), and 3rd run (blue). Glass transition temperatures are indicated by arrows and summarized in Table S1.

Table S3. Thermomechanical properties as determined from BLS experiments.

Sample	Particles			Film		
	T_g (K)	α_g ($-10^{-4}K^{-1}$)	α_m ($-10^{-3}K^{-1}$)	T_g (K)	α_g ($-10^{-4}K^{-1}$)	α_m ($-10^{-3}K^{-1}$)
DP530	355±4	6.3±0.2	1.51±0.07	363±2	5.7±0.3	1.02±0.04
DP1170	353±3	6.6±0.6	1.62±0.03	360±3	5.9±0.5	1.01±0.01
DP1300	-	6.5±0.5	-	367±3	5.3±0.1	0.98±0.01
DP2480	-	9.2±0.6	-	356±3	4.0±0.1	1.00±0.02

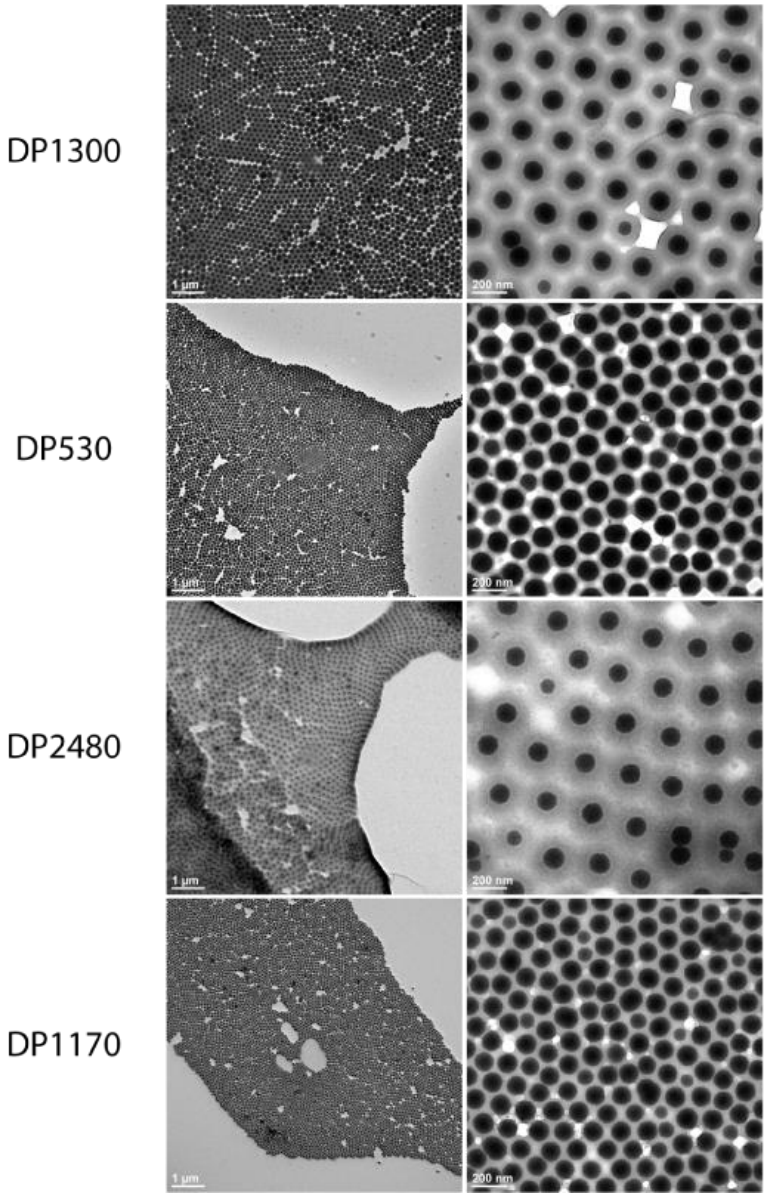

Figure S6. TEM images of particle brush films with scale bar 1µm (left panel) and 200 nm (right panel).

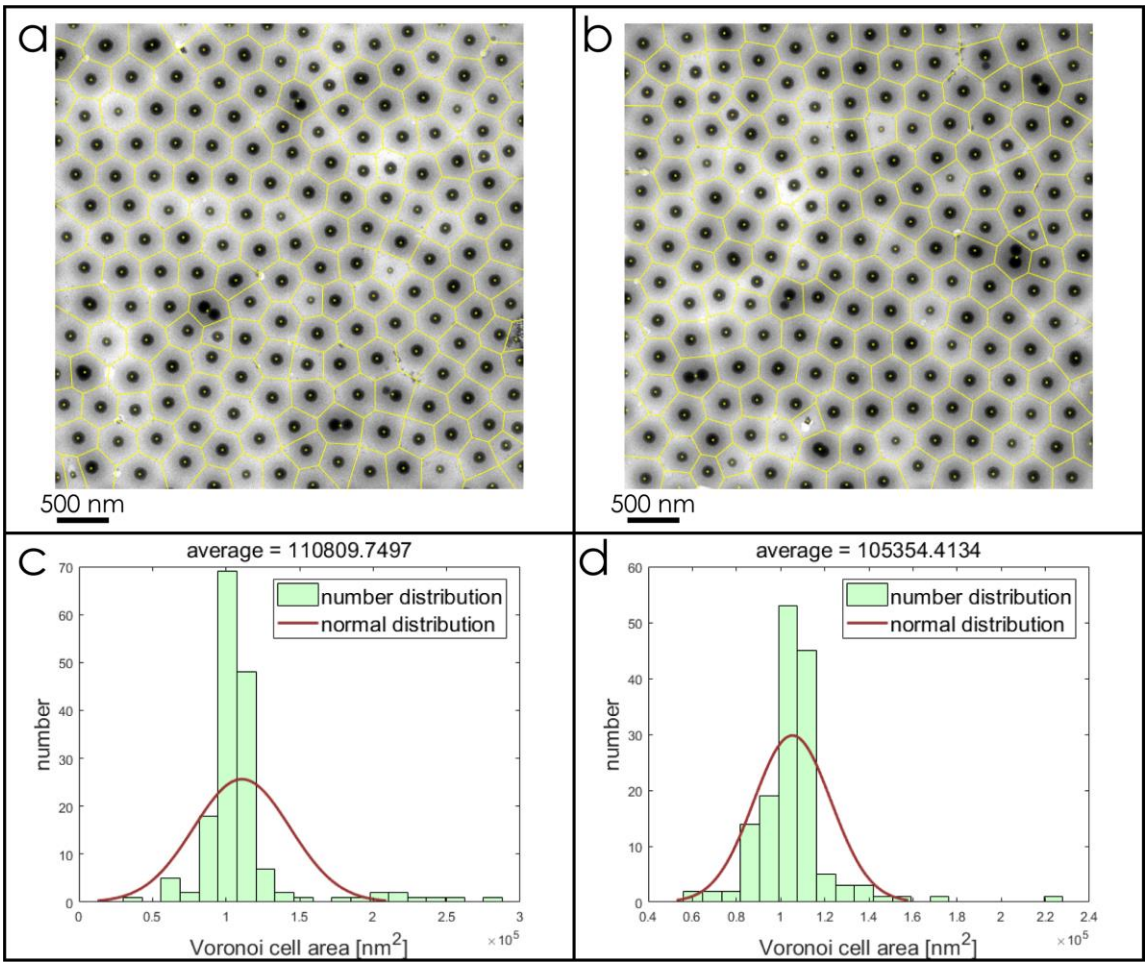

Figure S7. The TEM images show the microstructure of DP2480 (a) before and (b) after an annealing process. The annealing process was taken at 130 ^{o}C for 2h. The corresponding distributions of areas of Voronoi cell elements (marked in the TEM images with yellow polygon) (c) before and (d) after the annealing process were shown in histograms. The normal distribution (red line in figure c and d) is fitted with Gaussian distribution to estimate the deviation. The similar microstructure in the TEM images and average area suggest no structural changes after the thermal annealing process.

Table S4. The parameters A and B of particle brush films.

Sample	A×10^3 (m/s) (T<T_g)	B×10^5 (mK/s) (T<T_g)	A×10^3 (mK/s) (T>T_g)	B×10^5 (mK/s) (T>T_g)
DP1300	-1.7	2.0	0.2	9.1
DP2480	-1.9	1.5	0.06	8.0
DP530	-1.9	2.6	0.3	10.5
DP1170	-2.1	2.8	0.2	10.9
PS-30K	-1.9	1.4	0.6	10.5

A and B are the intercept and slope in the equation. ($c_L = \frac{B}{T} - A$)