Supporting Information

Linear Viscoelastic Response of Unentangled Polystyrene Bottlebrushes

Stelios Alexandris^{1*}, Katerina Peponaki^{1,2}, Paraskevi Petropoulou³, Georgios

Sakellariou³, Dimitris Vlassopoulos^{1,2}

FORTH, Institute of Electronic Structure and Laser, Heraklion, Crete, Greece ²University of Crete, Department of Materials Science and Technology, Heraklion, Crete, Greece ³National and Kapodistrian University of Athens, Department of Chemistry, Greece

- I. Dynamic light scattering characterization
- II. Determination of glass temperature (DSC and rheology)
- III. Dynamic rheological data and analysis
- IV. Estimation of bottlebrush entanglement molar mass
- V. Estimation of the backbone degree of polymerization for a bottlebrush polymer (side-chain molar mass=5k) with L/D=1
- VI. Carreau fit parameters
- VII. Description of the linear viscoelastic spectra

I. Dynamic light scattering characterization



Figure S1. (a) Normalized time autocorrelation function of the scattered intensity for 132k-5k PS bottlebrush in toluene, in dilute solution at θ =90° and 20°C. (b) Translational diffusion coefficient in a Zimm representation. The value of the intercept is 5.03x10⁻⁷ cm²/s and the resulting hydrodynamic radius is R_h =5 nm.



Figure S2. Zimm plots for largest 769k-7k (top) and smallest 132k-5k (bottom) PS bottlebrushes in toluene at 20°C.

II. Determination of glass temperature (DSC and rheology)



Figure S3. DSC heating curves of the four bottlebrush PS and the two linear PS. The arrows indicate the T_g midpoint values of a bottlebrush and a linear PS. Curves are second heating scans at 10 K/min.



Figure S4. Temperature dependence of storage and loss moduli and tan δ for bottlebrush PS. The two dashed vertical lines denote the peak of tan δ and the moduli crossover at high frequencies.

III. Dynamic rheological data and analysis



Figure S5. Dynamic master curves of *G'* (closed symbols) and *G''* (open symbols) for linear and bottlebrush PS along with the conversion of creep compliance measurements into dynamic moduli at a temperature $T_{ref}=T_g+36^{\circ}$ C. The four arrows show the moduli values that correspond to the distinct relaxation regions observed in the van Gurp-Palmen plot for 769k-7k bottlebrush.



Figure S6. Master curves of the loss tangent (*tan* δ) for linear and bottlebrush PS at T_{ref} =110°C.



Figure S7. Dynamic master curves of G' (closed symbols) and G'' (open symbols) for bottlebrush PS along with the conversion of creep compliance measurements into dynamic moduli. The extraction of

terminal times from the lines with slopes of 1 and 2 are shown. For the 191k-5k and 769k-7k bottlebrushes, the faster terminal times (black arrows) are shown as well. These times become more separated as the total molar mass increases (see manuscript).



Figure S8. Steady state recoverable compliance vs total molar mass of the bottlebrushes. A line with slope 1 is also shown (see main text).

IV. Estimation of bottlebrush entanglement molar mass

To find M_e (eq. S1) we need to know the following parameters (see also Table S1)¹: i) the packing length p (which is a measure of the relative thickness of a chain and a parameter that links the conformational properties of flexible chains to their viscoelastic properties), ii) the reptation tube diameter d_t through the Ronca-Lin parameter, η_t , iii) the density ρ of the polymer and iv) the ratio $\langle R^2 \rangle / M$, where $\langle R^2 \rangle$ is the root mean square end to end distance and M is the total molar mass, as a function of the average molecular weight per backbone bond, m_b :

$$M_e = \eta_t^2 p^3 N_a \rho \tag{S1}$$

$$p = \frac{M}{\langle R \rangle^2 \rho N_a} \tag{S2}$$

$$\frac{\langle R \rangle^2}{M} \cong 40 m_b^{-1.3}$$
(S3)

$$\eta_t \approx \frac{d_t}{p} \tag{S4}$$

The value of the entanglement molar mass (see Table S1) for the bottlebrush is: $M_e \approx 4 \times 10^7$ g/mol.

parameter	value
<r>²/M (m)</r>	3.9×10^{-4}
d _t (m)	76.5×10^{-10}
p (m)	428×10^{-9}
η _t	0.017
M_e (g/mol)	4x10 ⁷

Table S1. Values of extracted parameters from bottlebrush entanglement analysis: packing length, *p*, reptation tube diameter, d_t , Ronca-Lin parameter, η_t and ratio $\langle R^2 \rangle /M$ for 769k-7k.

V. Estimation of L/D ratio and backbone degree of polymerization for a bottlebrush polymer (side-chain molar mass=5k) with L/D=1

 M_n =5000 (g/mol) =104 (g/mol) x $n \rightarrow n$ =48

Radius of bottlebrush: R=0.25nm x (1/2+n)=12.125 nm

Respective radius of gyration of side chain (for reference):

 $R_g = \frac{1.8X \left(\frac{M_n}{720}\right)^{1/2}}{\sqrt{6}} = 1.9 \text{ nm (PS: Kuhn length} = 1.8 \text{ nm, Kuhm molar mass} = 720 \text{ g/mol}).$ Diameter: D=2R=24.25 nmLength per backbone monomer: $L_{repeat unit}=0.25 \text{ nm}$ $L=n_{bb}X L_{repeat unit}.$ Example for 132k-5k: L=6.5 nm, L/D=0.26 (see also Table 1 of main text). Degree of polymerization of a bottlebrush with L/D=1: $L/L_{repeat unit}=D/L_{repeat unit}=97$.

VI. Carreau fit parameters

Table S2. Parameters from Carreau model fit of the complex viscosity curves for 132k-5k, 292k-5k, 191k-5k and 769k-7k bottlebrush polystyrenes (see main text)

Code	η_0 (Pas)	τ (s)	n
132k-5k	55221	2.1	0.11
191k-5k	119434	49.4	0.13
292k-5k	156187	171	0.14
769k-7k	579376	36187	0.14

VII. Description of the linear viscoelastic spectra

To analyze the entire viscoelastic spectrum we use a generalized Maxwell model:

$$G'(\omega) = \sum_{l=1}^{N} \frac{G_{0l} \omega^2 \tau_{Rl}^2}{1 + \omega^2 \tau_{Rl}^2}$$

$$G''(\omega) = \sum_{l=1}^{N} \frac{G_{0l} \omega \tau_{Rl}}{1 + \omega^2 \tau_{Rl}^2}$$
(S5)

where G_0 and τ_R are fitting constants (see Table S3). Fig. S9 depicts the data of the three bottlebrushes (132k-5k, 191k-5k and 769k-7k) along with fits of eq. S5 with N=6-8 Rouse modes but without accounting for segmental dynamics (red dashed lines). In order to obtain a good description of the high frequency behavior, a phenomenological approach has been proposed by Benallal et al.^{2,3,4}. It consists of adding an extra relaxation process corresponding to the glass transition and it was described by using a Davidson-Cole equation, whose Fourier transform if given by $G_{HF}(t)=G_{\infty}(1-erf(t/\tau_0)^{1/2})$, where τ_0 is the segmental time and G_{∞} the glassy modulus (Fig. S9 insets and Table S4).







Figure S9. Shifted storage and loss moduli versus shifted frequency at T_{ref} =110 °C for (a) 132k-5k PS, (b) 191k-5k and (c) 769k-7k: comparison between experimental (symbols) and theoretical (dashed line) data (eq. S5). Inset: Respective representation at high frequencies in the glassy regime (data fitted with the phenomenological function $G_{HF}(t)$).

Parameter/mode	132k-5k	191k-5k	769k-7k
G ₀₁	254825.3	181547.2	0.011
G ₀₂	242737.9	1157.6	10.2
G ₀₃	112965.8	541496.6	311.6
G ₀₄	2.4×10^{7}	38800.4	3861.34
G ₀₅	491006.8	272270.5	37443.1
G ₀₆	56184.8	1.6	144456
G ₀₇	-	-	508393
G ₀₈	-	-	2.1x10 ⁶
τ_{R1}	0.02	-0.16	62255.2
τ _{R2}	0.08	13.14	5950.1

Table S3. Maxwell fit parameters for 132k-5k, 191k-5k and 769k-7k bottlebrushes

τ _{R3}	0.35	-0.0058	568.7
τ_{R4}	$1.7 \text{x} 10^{-4}$	1.07	54.4
τ_{R5}	0.0045	0.036	5.2
τ_{R6}	0.35	541.5	0.49
τ_{R7}			0.047
$ au_{R8}$			0.0045

Table S4. Error function fit parameters for 132k-5k, 191k-5k and 769k-7k bottlebrush polystyrenes

parameters	132k-5k	191k-5k	769k-7k
$\tau_0(s)$	0.12	0.14	0.13
G∞ (Pa)	2.53x10 ⁸	2.63×10^8	8.8x10 ⁸

References

- 1. Fetters L., Lohse, D., Garcia-Franco C., Brant, P., Richter D. Prediction of melt state Poly(R-olefin) rheological properties: the unsuspected role of the average molecular weight per backbone bond. *Macromolecules* **2002**, *35*, 10096-10101.
- 2. Benallal A., Marin G., Montfort J., Derail C. Linear viscoelasticity revisited: the relaxation function of monodisperse polymer melts. *Macromolecules* **1993**, *26*, 7229-7235.
- 3. Santangelo P., Roland C. Interrupted shear flow of unentangled polystyrene melts. *J. Rheol.* **2001**, *45*, 583.
- 4. Van Ruymbeke E., Muliawan E., Vlassopoulos D., Gao H., Matyjaszewski K. Melt rheology of star polymers with large number of small arms, prepared by crosslinking poly(n-butyl acrylate) macromonomers via ATRP. *Eur. Phys. J.* **2011**, *47*, 746-751.