Supporting Information

Power Law Relaxations in Lamellae Forming Brush Block Copolymers with Asymmetric Molecular Shape

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Experimental Section

Synthesis:

The synthesis of (polynorbornene-g-poly(styrene)) ((PS-NB 2.9k)_n) and (polynorbornene-g-poly(ethylene oxide)) (PEO-NB 5k)_m) macromonomers as well as PS-b-PEO bottlebrush block copolymers followed the established routine in previous publication.\textsuperscript{1,2} Molecular weights were controlled by varying catalyst-to-monomer ratio during the polymerization reaction. Mass fractions were kept constant by including equal amounts of PS-NB and PEO-NB macromonomers into each synthesis reaction.

General Methods:

\textit{\textsuperscript{1}H NMR spectroscopy} was recorded in CDCl\textsubscript{3} using a Brucker Avance DPX 300 NMR Spectrometer. Gel permeation chromatography (GPC) of the bottle brush copolymers was carried out in two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a Wyatt DAWN EOS multangle laser light scattering (MALLS) detector and a Wyatt rEX RI detector. THF + 1 vol. % triethylamine (TEA) was used as the eluent at a flow rate of 1 ml/min. No calibration standards were used for the bottle brush copolymers molecular weight determination, and \textit{dn/dc} values were obtained for each injection by assuming 100% mass elution from the columns. Dispersity was calculated based on linear PS standard calibration. GPC of macromonomers side chains was carried out using an Agilent 1200 instrument with two 5 μm mixed-D columns, a 5 μm guard column, and a RI detector (HP1047A). THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for the calibration. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q100 DSC equipped with an RCS cooling system and nitrogen gas purge with a flow rate of 50 mL/min. All measurements were conducted in the temperature range of -50 to 120 °C at a constant heating and cooling rate of 10 °C/min under a nitrogen atmosphere.
Equations/Calculations:

Volume Fraction Calculation:

The mass ratio of PS and PEO blocks was calculated according to the corresponding molar ratio as determined using $^1$H-NMR spectra (PS phenyl group (6.5-7.2 ppm, 5H per unit) and PEO backbone (3.6-3.8 ppm, 4H per unit)). Subsequently, the theoretical volume ratio of PS and PEO in the block copolymer ($V_{PS}/V_{PEO}$) was obtained using their estimated bulk densities (1.05 g/cm$^3$ and 1.09 g/cm$^3$ for PS and PEO, respectively). The volume ratio was determined as follows:

$$
\frac{V_{PS}}{V_{PEO}} = \frac{A_{PS} \cdot M_{PS}}{5 \cdot \rho_{PS}} \left/ \frac{A_{PEO} \cdot M_{PEO}}{4 \cdot \rho_{PEO}} \right.
$$

Where the $V_{PS}$ and $V_{PEO}$ were the volume of PS and PEO block accordingly; the $A_{PS}$ and $A_{PEO}$ were integrations of corresponding signals in $^1$H-NMR spectra; $M_{PS}$ and $M_{PEO}$ were molecular weight per repeat unit, 104 g/mol for PS and 44 g/mol for PEO respectively. The PEO domain volume fraction was calculated as $f_{PEO} = V_{PEO} / (V_{PEO} + V_{PS})$.

Dense Brush Limit:

Bottlebrushes with large $z$ often reside in the “dense brush” (DB) limit. The DB limit is achieved when the size of the side chain (radius of gyration $R_g$) is larger than the length between backbone repeat units ($L_g$). At a graft density of $z = 1$, $L_g$ is equal to the length of one norbornene unit ($L_g = 0.62$ nm, or 6.2 Å).$^3$ $R_g$ for an unperturbed Gaussian coil is calculated according to Eq. S2

$$
R_g = a \sqrt{\frac{N}{6}}
$$

Where $a$ is the statistical segment length and $N$ is the degree of polymerization. For the PS side chains, $a_{PS} = 6.7$ Å and $N = 28$. This gives a value of $R_g(PS) = 14.5$ Å. For the PEO side chains, $a_{PEO} = 6.0$ Å and $N = 114$. This gives a value of $R_g(PEO) = 26.2$ Å. Therefore, $2R_g >> L_g$ for both the PEO and PS blocks.
Comparison of PS block & PEO block macromolecular features

Side Chains

Despite the dense chain packing, the side chains do not stretch significantly more than their unperturbed Gaussian conformation. Therefore, the average end-to-end distance \( R_{sc} \) scales with \( N_{sc}^{1/2} \). We can calculate the side chain size from the relationship \( R_{sc} = aN_{sc}^{1/2} \), where \( a \) is statistical segment length. Using the previously reported values for \( a \), \( R_{sc, PS} = 3.55 \) nm and \( R_{sc, PEO} = 6.41 \) nm respectively.

Backbone

For bottlebrushes in the melt, the backbone is depicted as a worm-like chain defined by the contour length \( L \) and persistence length \( l_p \). The contour length \( (L) \) of the backbone is defined as \( L = L_g^{*}N_{bb} = (0.62 \text{ nm})^{*}N_{bb} \). Contour lengths for all dbBB samples are calculated in Table S1. For each block, the backbone is additionally stiffened by the side chains. If \( (R_{sc, PEO}) > (R_{sc, PS}) \), we can conclude that the PEO backbone is stiffer than the PS backbone \( (l_{p, PEO} > l_{p, PS}) \).

Table S1. Contour Lengths of dbBB blocks

| \( N_{bb} \) | \( L_{(bb, PS)} \) (nm) | \( L_{(bb, PEO)} \) (nm) | \( L_{(bb)} \) (nm) |
|-------------|-----------------|-----------------|-----------------|
| 21          | 8.1             | 4.9             | 13              |
| 40          | 15.5            | 9.3             | 24.8            |
| 55          | 21.1            | 13              | 34              |
| 72          | 27.9            | 16.7            | 44.6            |
| 119         | 45.9            | 27.9            | 73.8            |

\( ^a \) Overall backbone degree of polymerization \( (N_{bb}= N_{bb, PEO} + N_{bb, PS}) \) calculated using absolute molecular weights and \( D \) as measured by GPC and mass fraction from NMR. \( ^b \) Contour length of PS block \( (L_{(bb, PS)}) \), PEO block \( (L_{(bb, PEO)}) \), and total dbBB \( (L_{(bb)}) \) calculated using equation \( L = (0.62 \text{ nm})^{*}N \).
**Dual Power Law Model**

The dual power law model represents the relaxation time spectrum $H(\tau)$ as a linear superposition of two single power law modes. Here, $H(\tau)$ is defined from the relaxation modulus $G(t)$ according to Eq. S3, which is evaluated for all $\tau < \tau_{\text{max}}$. Various forms are proposed to model a wide range of material responses. Eq. S4 and S5 are used in the case of $n_1 > n_2$. A cutoff at $\tau_{\text{max}}$ is applied when fitting the dual power law model (specifically Eq. S4) to the continuous spectrum calculated for the dbBB samples. As a result, $H(\tau) = 0$ for all modes where $\tau > \tau_{\text{max}}$ and $H_0$ is effectively 0.

$$G(t) = \int_0^{\tau_{\text{max}}} \frac{d\tau}{\tau} H(\tau) e^{-t/\tau}$$ \hspace{1cm} \text{Eq. S3}

$$H(\tau) = H_0 + H_1 \left(1 + \frac{\tau}{\tau_1}\right)^{-n_1} + H_2 \left(1 + \frac{\tau}{\tau_2}\right)^{-n_2}$$ \hspace{1cm} \text{Eq. S4}

$$H(\tau) = H_0 + \frac{H_1}{1 + \left(\frac{\tau}{\tau_1}\right)^{n_1}} + \frac{H_2}{1 + \left(\frac{\tau}{\tau_2}\right)^{n_2}}$$ \hspace{1cm} \text{Eq. S5}

**Table S2.** Parameters for Dual Power Law Model fit in Figure 6:

| $H_0$ | $H_1$ (Pa) | $\tau_1$ (s) | $n_1$ | $H_2$ (Pa) | $\tau_2$ (s) | $n_2$ | $\tau_{\text{max}}$ (s) |
|-------|-----------|--------------|-------|------------|--------------|-------|-----------------|
| ~0 | 4.0 x10^6 | 2.9 x10^{-3} | 0.83 | 8 x10^4 | 3.25 x10^{-1} | 0.67 | 1 x10^4 |

Eq. S6 and Eq. S7 are presented as the inverse linear superposition of two single power law modes in the case that $n_1 < n_2$.

$$H(\tau) = \frac{H_3 \left(1 + \frac{\tau}{\tau_3}\right)^{-n_1} \left(1 + \frac{\tau}{\tau_2}\right)^{-n_2}}{H_1 \left(1 + \frac{\tau}{\tau_1}\right)^{-n_1} + H_2 \left(1 + \frac{\tau}{\tau_2}\right)^{-n_2}}$$ \hspace{1cm} \text{Eq. S6}

$$H(\tau) = \frac{H_1 \left(1 + \frac{\tau}{\tau_1}\right)^{n_1} \left(1 + \frac{\tau}{\tau_2}\right)^{n_2}}{H_3 \left(1 + \frac{\tau}{\tau_3}\right)^{n_1} + H_2 \left(1 + \frac{\tau}{\tau_2}\right)^{n_2}}$$ \hspace{1cm} \text{Eq. S7}
Supplementary Figures

Figure S1. $^1$H NMR of a) PS-NB and b) PEO-NB macromonomers. c) Characteristic $^1$H NMR of PS-$b$-PEO brush block copolymer sample. $^1$H-NMR of synthesized dbBBs shows signal from PEO ($\delta = 3.6$-$3.8$ ppm) and PS ($\delta = 6.5$-$7.2$ ppm) side chain protons respectively. The absence of a peak at $\delta = 5.04$-$5.38$ ppm (corresponding the protons on the norbornene functionalized end) indicates the complete polymerization of ROMP macromonomers.
Figure S2. GPC RI traces of the a) PS-NB and b) PEO-NB macromonomers, c) the series of brush block copolymers. In-line $dn/dc$ values calculated assuming 100% mass elution (theoretical $dn/dc \approx 0.116$ ml/g)

Figure S3. 2D X-Ray Scattering Patterns of microphase separated dbBB materials at room temperature. Anisotropic scattering patterns indicate some degree of domain orientation and long range ordered morphology.
**Figure S4.** Domain spacing ($d_0$) of lamellar morphology calculated from SAXS vs. Backbone degree of polymerization ($N_{bb}$) for dbBB series. Dotted lines follow power law fits to relationship $d_0 \sim N_{bb}^\alpha$. Fit to dbBB-21, dbBB-40, and dbBB-55 is $\alpha = 0.36$ ($R^2 = 0.99$, std. err. ± 0.02). In this regime, the lamellar spacing is dominated by the side chain length, which is comparable to the backbone length. This phenomenon was described by Dalsin et al. for PS-$b$-aPP dbBBs with short backbone length. 3 Fit to dbBB-40, dbBB-55, dbBB-72, and dbBB-119 is $\alpha = 0.84$ ($R^2 = 0.96$, std. err. ± 0.12). In the larger $N_{bb}$ regime, the scaling depicts an extended backbone conformation when compared to a scaling of $\alpha = 0.66$ expected for LBCPs in the strong segregation limit. The scaling factor is in close agreement with observations by Gu et al. on the scaling of $d_0$ for a system of PS-$b$-PLA dbBBs ($\alpha = 0.93 & 0.82$ for systems with short and long side chains respectively). 5
Figure S5. Trends in a) Intensity of $q^*$, b) Full width at half maximum (fwhm) of $q^*$, and c) d-spacing as a function of temperature. Data compiled from temperature controlled SAXS experiments.
Figure S6. SAXS spectra of dbBB after cooling down to room temperature from $T = 200 \, ^\circ C$.

Figure S7. Time Temperature Superposition shift factors $a_T$ (horizontal) and $b_T$ (vertical) at $T = 120 \, ^\circ C$ normalized with respect to $T_g$: $(T - T_g)/T_g$. Lines show fit to WLF equation: $\log(a_T) = C_1(T-T_{ref})/(C_2+(T-T_{ref}))$. Shift factors $b_T$ were determined to be close to 1. Temperature dependence in $a_T$ varies slightly with $N_{bb}$ due to heterogeneous nature of the polymeric architecture and morphology.
Figure S8. a) Heating and cooling DSC traces of dbBB series, indicating melting and crystallization of PEO b) Expanded view of glass transition of PS block. \( T_g \) is reported in °C. Qualitatively, \( T_g \) is depressed when compared to that of bulk PS (\( T_g \approx 100 \) °C). The reduction in \( T_g \) from bulk PS is due to the low MW chains as well as the additional confinement of the chains at one end (i.e. connection to the backbone). Overall, \( T_g \) of PS domain increases with \( N_{bb} \) from \( T = 86 \) to 94 °C.

Figure S9. Various viscoelastic functions of dbBB dynamic response: a) Booij-Palmen plot, b) Normalized Loss Modulus (\( G''/G^* \) vs. \( \omega \)) c) Complex viscosity (\( \eta^* \)) vs. complex modulus (\( G^* \))
**Figure S10.** Individual fits of dual power law model (Eq. S7) to calculated $H(\tau)$ for each dbBB sample. Parameter for fit are presented in Table S3.

**Figure S11.** a) Comparison of measured dynamic data (circles) and calculated data (line) from dual power law spectrum for dbBB-55. Complex viscosity vs shifted frequency is displayed. b) Linear superposition of two single power law functions (dotted lines) at short and long time to form dual power law model (solid blue line) fit to experimental data (circles).
Figure S12. Master curves of reduced complex viscosity ($\eta^*$) versus shifted frequency ($a_T\omega$) described by a power law scaling of $\eta^*(\omega) \sim \omega^\alpha$. Distinct regimes are consistently present across all $N_{bb}$. In the high frequency limit, while all curves do not superimpose, the scaling is approximately $\alpha \approx 0.75$ in each case. Scaling of $\alpha \approx 0.33$ was observed in the transition from the highest frequency to the intermediate regime ($a_T\omega \sim 10^4 \text{rad/s}$), followed by $\alpha \approx 0.5$ in the intermediate ($a_T\omega < 10^5 \text{rad/s}$), and returns to $\alpha \approx 0.33$ at terminal timescales. The quantitative scaling is remarkably comparable to that identified by Dalsin et al. for hBBs. However, the terminal regime contrasts the hBBs response, where $\eta^*(\omega)$ plateaus and a zero-shear viscosity ($\eta_0$) is ultimately resolved. The viscoelastic terminal behavior suggests that there are consequences of the microphase separated structure that are unique to the dbBBs.
Figure S13. Data of Haugan et al.; dynamic data of poly(lactide) (PLA) homopolymer bottlebrushes (hBBs) with side chain $M_n = 3.5$ kg/mol, graft density $z = 1$ and backbone degree of polymerization ranging from $N_{bb} = 12 - 2900$. Relaxation Time Spectra $H(\tau)$ calculated from dynamic data at reference temperature of $T_{ref} = T_g + 34 \degree$C. Spectra appear to follow single power law model with form $H(\tau) = H_0(\tau)^n$ and power law exponent of $n = 0.6$, remarkably like a critical gel. In comparison to dbBBs, the hBBs do not exhibit microphase separation, and show a single relaxation mode.

References:

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