Supporting Information for

Main-Chain Stiffness of Cellulosic Bottlebrushes with Polystyrene Side Chains Introduced Regioselectively at the O-6 Position

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1. Synthesis of PSt-N$_3$

**Materials.** Styrene (St, 99 %, Nacalai Tesque, Inc., Kyoto, Japan) was purified through an alumina column. Copper(I) bromide (CuBr) (99.9 %, Wako Pure Chemicals, Osaka, Japan) was purified by stirring in acetic acid over 24 h, followed by filtration, washing with ethanol and diethyl ether, and then drying under vacuum. Ethyl 2-bromoisobutyrate (EBiB, 98 %, Tokyo Chemical Industry. Co., Tokyo, Japan) and other reagents and solvents (Wako) were of the highest grade available and used without further purification.

**Measurements.** Nuclear magnetic resonance (NMR) spectra (600 MHz) were recorded on an AVANCE III 600 instrument (Bruker, Billerica, MA, USA) using CDCl$_3$. Chemical shifts, relative to tetramethylsilane (TMS) as an internal standard, are given in $\delta$ values. Size-exclusion chromatography (SEC) analysis for PSt samples was carried out at 40 °C on a Shodex GPC-104 high-speed liquid chromatography system (Showa Denko K.K., Tokyo, Japan) equipped with a KF-G (Shodex) guard column, two KF-404 HQ (Shodex) columns, and a SPD-20A UV detector (Shimadzu, Kyoto, Japan). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.3 mL min$^{-1}$. PSt standards were used to calibrate the SEC system.

**PSt-Br.** General procedure: EBiB (0.113 g, 0.58 mmol) and 4,4′-dinonyl-2,2′-bipyridine (dNbipy, 0.5185 g, 1.27 mmol) were dissolved in St (18.0 g, 76.8 mmol). After the solution was purged with Ar gas for 10 min, CuBr (0.0769 g, 0.54 mmol) and copper(II) bromide (CuBr$_2$) (0.0900 g, 0.040 mmol) were added into the solution under Ar atmosphere. The mixture was stirred at 90 °C for 6 h. After the polymerization, the solution was diluted with approximately 20 mL CH$_2$Cl$_2$ and poured into methanol (800 mL). The precipitate was collected and washed with methanol. The product was dried under vacuum at 60 °C (3.98 g). SEC: $M_n = 6.2 \times 10^3$ g mol$^{-1}$, $M_w/M_n = 1.09$. $^1$H NMR
PSt-N$_3$. Azide substitution at the PSt terminal was conducted according to Matyjaszewski and coworkers.$^8$ General procedure: PSt-Br (3.40 g, 0.55 mmol) and sodium azide (0.378 g, 5.8 mmol) were dissolved in DMF (35 mL) and stirred at rt for 2 d. The reaction mixture was diluted with CH$_2$Cl$_2$ (4 mL) and poured into methanol. The precipitate was filtered and washed with a mixture of methanol and water (9:1, v/v). The final product was dried under vacuum at 60 °C overnight (3.29 g, 93%). SEC: $M_n = 6.4 \times 10^3$ g mol$^{-1}$, $M_w/M_n = 1.10$. $^1$H NMR (600 MHz, CDCl$_3$): 0.8–1.1 (–CH$_2$–CH$_3$, –C–(CH$_3$)$_2$), 1.2–2.5 (–CH$_2$–C$_6$H$_5$–), 3.3–3.7 (OCH$_2$–), 4.3–4.6 (–CH$_2$–Br), 6.3–7.5 (arom. H). Azidation was estimated to be over 95%.

2. Monitoring Click Reaction by SEC.

The click reaction was monitored by SEC using a Tosoh GPC system equipped with a CCPS pump (Tosoh Corp., Tokyo, Japan), KF-G guard column (Shodex), two KF-806L columns (Shodex), a CO-8020 column oven (Tosoh) at 40 °C, and a UV-8020 UV detector (Tosoh, wavelength: 254 nm). THF with triethylamine (0.5 v%) was used as the eluent at a flow rate of 0.8 mL min$^{-1}$.
3. Supporting Figures

**Figure S1.** $^1$H NMR spectra of 1a (a), 1b (b), and 1c (c) (CDCl$_3$, rt, 600 MHz).
**Figure S2.** The dependence of \( \log \left( \langle S^2 \rangle_M / DP_w \right) \) on \( \log(DP_w) \) for (a) 1a, (b) 1b, and (c) 1c. The red curves represent the theoretical value of the unperturbed KP chain model with the determined \( \lambda^{-1} \) values listed in Table 2, whereas the blue and yellow curves represent the theoretical value of the KP chain model with the determined \( \lambda^{-1} \) values plus 1 and minus 1, respectively.
### 4. Supporting Table

**Table S1.** Model parameters of the first order perturbation theory for PSt-PSt bottlebrush\textsuperscript{S2} and hypothetic PSt-PSt bottlebrush.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\lambda_0^{-1}$ (nm)</th>
<th>$h$ (nm)</th>
<th>$b$ (nm)</th>
<th>$\beta_3 \times 10^{-3}$ (nm(^6))</th>
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</thead>
<tbody>
<tr>
<td>PSt-PSt bottlebrush</td>
<td>8</td>
<td>0.27</td>
<td>0.74</td>
<td>4</td>
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<tr>
<td>hypothetic PSt-PSt bottlebrush</td>
<td>8</td>
<td>0.52</td>
<td>0.74</td>
<td>4</td>
</tr>
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</table>
5. Supporting References
