Versatile Strategies to Tailor the Glass Transition Temperatures of Bottlebrush Polymers

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Supporting Information

Table of contents

EXPERIMENTAL PROCEDURES	3
General information	3
Synthesis of oligo(styrene) (oSty) via ATRP	4
Synthesis of ω-norbornenyl oligo(styrene) (NB-oSty)	5
Synthesis of disperse (BBP) and discrete (PBP) bottlebrush homopolymers	7
Synthesis of bottlebrush block copolymers (b-PBP)	7
CHARACTERIZATION DATA	9
Figure S1. ¹ H NMR spectra of disperse oSty4 and disperse oSty4-OH	9
Figure S2. ¹ H NMR and ¹³ C NMR spectra of disperse NB-oSty4	10
Figure S3. ¹ H NMR and ¹³ C NMR spectra of discrete NB-oSty2 (S2)	11
Figure S4. ¹ H NMR and ¹³ C NMR spectra of discrete NB-oSty4 (S4)	12
Figure S5. ¹ H NMR spectra of discrete NB-oSty6 (S6)	13
Figure S6. ¹ H NMR and ¹³ C NMR spectra of discrete NB-oSty8 (S8)	14
Table S1. Disperse and discrete macromonomers used in this study	15
Figure S7. ¹ H NMR (500 MHz, CDCl ₃) of PBP-S2 ₂₂ and PBP-S2 ₃₆	16
Figure S8. ¹ H NMR (500 MHz, CDCl ₃) and ¹³ C NMR (125 MHz, CDCl ₃) of PBP-S4 ₃₀ .	17
Figure S9. ¹ H NMR (500 MHz, CDCl ₃) of PBP-S6 ₂₇	18
Figure S10. ¹ H NMR (500 MHz, CDCl ₃) of PBP-S8 ₃₂	18
Figure S11. ¹ H NMR (500 MHz, CDCl ₃) of b-PBP-S2 ₂₀ S8 ₁₀ and b-PBP-S8 ₂₀ S2 ₁₀	19
Figure S12. ¹ H NMR (500 MHz, CDCl ₃) of b-PBP-S8 ₅ S2 ₂₀ S8 ₅ and b-PBP-S8 ₁₀ S2 ₁₀ S8 ₁₀	20
Figure S13. SEC trace of disperse NB-oSty4 and the isolated macromonomer libraries (S2–S8)	22
Figure S14. MALDI-ToF spectra of discrete macromonomers S3, S4, S5, S6, S7, and S8	23
Figure S15.FTIR spectra of NB-oSty4, S2, S4, and S8	24
Figure S16. FTIR spectra of PBP-S4 ₃₀ and b-PBP-S2 ₂₀ S8 ₁₀	25
Figure S17. SEC traces of PBP-S8, PBP-S6, PBP-S4, and PBP-S2 bottlebrush series	26
Figure S18. Glass transition temperature (T_g) of discrete macromonomers S2 - S8	27
Figure S19. DSC traces of PBP-S8, PBP-S6, PBP-S4, and PBP-S2 series	28
Table S2. Bottlebrush polymers synthesized and used in this study	29
Figure S20. Glass transition temperature (T_g) of discrete macromonomers S2 - S8	31
Figure S21. DSC traces of PBP-S8, PBP-S6, PBP-S4, and PBP-S2 series	32
Figure S22. Exponential fitting to determine N_{BB}^* for PBP-S8, -S6, -S4, and -S2	33
Figure S23. DSC traces of PBP-S2 ₃₀ , PBP-S8 ₃₀ and multiblocks	34
Table S3. T_g prediction of multiblocks from Fox equation	35
GLASS TRANSITION BLENDING THEORIES	35

EXPERIMENTAL PROCEDURES

General information

All reagents were purchased from Sigma-Aldrich/Millipore and used without further purification unless stated otherwise. Copper (II) bromide was purchased from Acros Organics. Styrene (Alfa Aesar, 99%) was passed through a plug of basic alumina to remove inhibitors prior to use. Solvents for chromatographic separations were purchased from VWR chemicals and used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

All reactions were carried out in oven-dried glassware under an inert atmosphere. Reactions were monitored with analytical thin-layer chromatography (TLC) using silica gel 60G F_{254} TLC plates from EMD Millipore and visualized using 254 nm UV, bromocresol green, or potassium permanganate. Automated flash chromatography of macromonomer was performed using a Biotage Isolera One unit equipped with an evaporative light scattering detector (ELSD, Teledyne ISCO). A reversed-phase C18 cartridge (60/120/400 g) and an acetonitrile/hexane gradient were used to separate the macromonomers. High-resolution separation of macromonomer was also performed using a preparative-scale recycling size-exclusion chromatography (rSEC, LaboACE LC-5060, JAIGEL2HR, and 2.5HR columns). Polymer samples (200–500 mg) were dissolved in ethanol-stabilized chloroform (eluent) and filtered before injection. The separation process was monitored in real time to isolate the desired fractions.

Gel permeation chromatography (GPC) was performed on a TOSOH HLC-8320GPC equipped with a TSKgel superH5000 column (3 µm particle and 20 nm pore size) eluting with tetrahydrofuran (THF). Absolute molecular weight analysis was performed using a Wyatt Dawn EOS multi-angle light scattering (MALS) detector ($\lambda = 658$ nm, Astra 6 software). Weight-averaged molecular weights (M_w) and number-averaged molecular weights (M_n) were calculated relative to linear polystyrene standards unless otherwise stated. ¹H and ¹³C Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance III 400 and 500 MHz spectrometers at 298 K. Chemical shifts (δ) are given in parts per million (ppm) and referenced using a deuterated solvent signal. MALDI-ToF-MS spectra were collected using a Bruker UltrafleXtreme tandem time-of-flight mass spectrometer in positive reflectron mode. Unless otherwise stated, MALDI spectra were collected using a 2,5-dihydroxybenzoic acid (DHB)/sodium trifluoroacetate (Na-TFA) matrix mixed with sample and deposited on a Bruker MTP 384-polished steel target plate.

MALDI analysis was performed using FlexAnalysis software. FT-IR spectra were collected on a Bruker Tensor 27 system equipped with a room temperature DTSG detector, a mid-IR source (4000 - 400 cm⁻¹), and a KBr beam splitter. Sample cell was a Pike Miracle single-bounce attenuated total reflectance (ATR) cell equipped with a ZnSe single crystal. Spectral resolution was set to 4 cm⁻¹ and 32 scans taken for each sample. Data was processed using Bruker OPUS software suites.

Glass transition of polymer samples was analyzed under nitrogen flow by Differential Scanning Calorimetry (DSC) on a TA Instruments Discovery DSC 250 equipped with a Refrigerated Cooling System RCS 90. The samples were cooled and heated at a rate of 10 °C/min for three heating and two cooling cycles, respectively. The third heating cycle was used for all analysis. Data analysis was performed on TA Instruments' Universal Analysis software. Glass transition temperatures (T_g) were determined from minima of the derivative of heat flow. To make the PBP-S2-PBP-S8 artificial blends, PBP-S2 and PBP-S8 were weighed separately, dissolved in chloroform, and mixed. Using a micropipette, the mixture was transferred to DSC pans, the solvent evaporated slowly under ambient conditions, followed by a vacuum evaporation in a vial connected to a Schlenk line. The third DSC scan was used to determine the T_g of each artificial blend.

Synthesis of oligo(styrene) using ATRP



То dried 40 mL vial. copper(I)bromide (CuBr) (0.5)an oven equiv.). N,N,N',N",Pentamethyldiethylenetriamine (PMDETA) (0.5 equiv.), and styrene (n equiv.) were added and sonicated for 10 min. Ethyl 2-bromoisobutyrate (EBiB) (1 equiv.) and a stir bar were added to the vial and degassed with Ar for 20 min. Removing the argon stream, the reaction proceeded at 90 °C while stirring until completion. Reaction progress was monitored via NMR analysis of aliquots taken at predetermined intervals. The polymerization was terminated by quenching with liquid nitrogen, exposing to the atmosphere, and diluting with chloroform. Catalyst was removed from the reaction mixture by passing through a plug of basic alumina, and excess solvent was reduced using rotary evaporation to obtain styrene oligomers (82% yield).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.29 – 6.45 (m, 18H), 4.60 – 4.35 (m, 1H), 3.78 – 3.41 (m, 2H), 2.78 – 2.20 (m, 3H), 2.18 – 1.46 (m, 8H), 1.18 – 0.78 (m, 6H 3H).

Synthesis of ω -hydroxyl-terminated oligo(styrene)



To an oven dried 40 mL vial, silver perchlorate (815mg, 3.94 mmol) was added and degassed for 20 min. Oligo(styrene) (2000mg, 3.28 mmol) was dissolved in acetone (20 mL) and degassed for 20 min. The degassed oligo(styrene) solution and excess DI water were added simultaneously to the vial, and the reaction was stirred overnight at room temperature.¹ After completion, the reaction was diluted with THF and passed through a plug of neutral alumina to remove the Ag salt. Excess solvent was reduced using rotary evaporation to obtain ω -hydroxyl oligo(styrene), and the crude sample was purified using column chromatography (Biotage Isolera One, SNAP Ultra) eluting with a gradient of hexane/ethyl acetate (1410 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.26 – 6.38 (m, 18H), 4.48 – 4.09 (m, 1H), 3.81 – 3.34 (m, 2H), 2.38 – 1.59 (m, 3H 8H), 1.19 – 0.75 (m, 6H 3H).

Synthesis of ω -norbornenyl oligo(styrene) macromonomer



Disperse NB-oSty4

In an oven dried 40 mL vial, exo-5-Norbornene-2-carboxylic acid (378 mg, 2.74 mmol) was dissolved in dichloromethane (8 mL). 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) (525 mg, 2.74 mmol) and dimethylaminopyridine (DMAP) (220 mg, 1.82 mmol) were added, and the mixture stirred. While stirring, ω -hydroxyl oligo(styrene) (1000 mg, 1.82 mmol) was added, and the reaction proceeded at room temperature for 24

h. Thin layer chromatography (TLC) was used to monitor reaction progress. The reaction was terminated by diluting with DCM. Excess solvent was reduced using rotary evaporation to obtain ω -norbornenyl oligo(styrene) macromonomers, and the crude sample was purified using column chromatography (Biotage Isolera One, SNAP Ultra) eluting with a gradient of hexane/ethyl acetate (929 mg, 76% yield).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.26 – 6.42 (m, 20H), 6.23 – 5.98 (m, 1H 1H), 5.67 – 5.19 (m, 1H), 3.82 – 3.38 (m, 2H), 3.04 – 2.77 (m, 1H 1H), 2.38 – 1.59 (m, 3H 8H), 1.19 – 0.75 (m, 6H 3H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 177.6, 175.0, 145.0, 138.0, 135.8, 128.3, 127.6, 126.0, 77.3, 73.9, 60.0, 46.5, 41.7, 30.0, 26.5, 14.0. $M_{n,MALDI-TOF}$ = 0.6 kDa, D = 1.16, $M_{n,NMR} = 0.6$ kDa. FT-IR (ATR, cm⁻¹): v = 3100 - 2800 (m; v_s (sp³, sp² C–H), 1720 (s; v_s (C=O)), 1180 (m; v_s (C-O)), 700 (s; v_b (sp² =C–H)).

Discrete macromonomers were obtained from chromatographic separation of disperse macromonomer

Discrete NB-oSty2 (S2)

¹H NMR (400 MHz, CDCl₃) δ ppm 7.26 - 7.00 (m, 10H), 6.18 – 6.04 (m, 1H 1H), 5.51 – 5.20 (m, 1H), 3.85 – 3.52 (m, 2H), 3.07 (d, *J* = 52 Hz, 1H), 2.92 (s, 1H), 2.29 – 1.80 (m, 2H 1H 2H), 1.16 – 0.94 (m, 6H 3H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 177.3, 177.8, 143.9, 141.4, 138.1, 135.8, 128.4, 125.9, 73.9, 60.1, 46.7, 41.9, 39.4, 30.4, 26.5, 25.4, 13.9. MS (MALDI-ToF): [M+Na]⁺ Calcd for C₃₀H₃₆O₄Na: 483.25, found: 483.27.

Discrete NB-oSty4 (S4)

¹H NMR (400 MHz, CDCl₃) δ ppm 7.26 – 6.72 (m, 20H), 6.20 – 5.99 (m, 1H 1H), 5.66 – 5.21 (m, 1H), 3.76 – 3.39 (m, 2H), 3.02 – 2.66 (m, 1H 1H), 2.36 – 1.59 (m, 3H 8H), 1.09 – 0.79 (m, 6H 3H). ¹³C NMR (125 MHz, CDCl₃): δ ppm 177.6, 175.0, 145.0, 137.9, 135.8, 128.1, 126.0, 73.8, 46.5, 43.4, 41.9, 40.2, 30.2, 26.5, 13.9. MS (MALDI-ToF): [M+Na]⁺ Calcd for C₄₆H₅₂O₄Na: 691.39, found: 691.46.

Discrete NB-oSty6 (S6)

¹H NMR (400 MHz, CDCl₃) δ ppm 7.26 – 6.44 (m, 30H), 6.20 – 5.97 (m, 1H 1H), 5.62 – 5.16 (m, 1H), 3.72 – 3.35 (m, 2H), 2.98 – 2.63 (m, 1H 1H), 2.54 – 1.56 (m, 5H 12H), 1.05 – 0.80 (m, 6H 3H). MS (MALDI-ToF): [M+Na]⁺ Calcd for C₆₂H₆₈O₄Na: 899.50, found: 899.48.

Discrete NB-oSty8 (S8)

¹H NMR (400 MHz, CDCl₃) δ ppm 7.25 – 6.36 (m, 40H), 6.19 – 5.98 (m, 1H 1H), 5.61 – 5.17 (m, 1H), 3.72 – 3.32 (m, 2H), 2.99 – 2.63 (m, 1H 1H), 2.54 – 1.53 (m, 7H 16H), 1.06 – 0.79 (m, 6H 3H). ¹³C NMR (125 MHz, CDCl3): δ

ppm 177.5, 174.9, 145.1, 138.1, 135.8, 128.0, 125.7, 73.8, 59.9, 46.3, 43.2, 41.6, 40.5, 30.4, 25.9, 24.9, 13.9. MS (MALDI-ToF): [M+Na]⁺ Calcd for C₇₈H₈₄O₄Na: 1107.64, found: 1107.41.

Synthesis of bottlebrush homopolymers using discrete and disperse macromonomers



Grubbs 3rd generation catalyst (G3) was prepared following reported procedures,² and DCM was degassed with Ar for 30 min prior to use.

To an oven-dried 4 mL vial equipped with a stir bar, NB-oSty macromonomer (m equiv.) was dissolved in DCM and degassed with Ar for 20 min. A degassed solution of Grubbs 3^{rd} generation catalyst (IMesH₂)(Cl)₂(C₃H₃N)₂Ru=CHPh (G3, 1 equiv, 100 mM) was injected into the mixture to initiate the polymerization. The mixture was stirred at room temperature for 30 min, and the polymerization was stopped by quenching with excess ethyl vinyl ether (EVE). The crude product was passed through a plug of basic alumina to remove the catalyst, and excess solvent was reduced in vacuo to obtain bottlebrush homopolymers (>90% yield).

Synthesis of multiblock bottlebrush polymers



b-PBP-S8_mS2_nS8_m (triblock structure)

Grubbs 3rd generation catalyst (G3) was prepared following reported procedures,² and DCM was degassed with Ar for 30 min prior to use.

To an oven-dried 4 mL vial equipped with a stir bar, S8 (1st block, m equiv.) was dissolved in DCM and degassed with Ar for 20 min. A degassed solution of G3 (1 equiv., 100 mM) was injected into the mixture to initiate the polymerization. The mixture was stirred at room temperature for 10 min, and an aliquot was collected. Degassed S2 solution (2nd block, n equiv.) was injected into the reaction mixture, and the mixture was stirred for an additional 10 min, and an aliquot was collected. Finally, degassed S8 solution (3rd block, m equiv.) was injected into the reaction mixture, and the mixture was stirred for an additional 10 min, and the mixture was stirred for an additional 10 min. The polymerization was stopped by quenching with excess ethyl vinyl ether (EVE). The crude product was passed through a plug of basic alumina to remove the catalyst, and excess solvent was reduced in vacuo to obtain a triblock bottlebrush polymer (> 90% yield).

CHARACTERIZATION DATA



Figure S1. ¹H NMR (400 MHz, CDCl₃) of **disperse oSty4-Br** and **oSty4-OH** (ω-hydroxyl oligo(styrene), avg. DP = 4).



Figure S2. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (125 MHz, CDCl₃) of **disperse NB-oSty4** (ω-norbornenyl oligo(styrene)).



Figure S3. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (125 MHz, CDCl₃) of discrete NB-oSty2 (S2).



Figure S4. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (125 MHz, CDCl₃) of S4.



Figure S5. ¹H NMR (400 MHz, CDCl₃) of S6.



Figure S6. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (125 MHz, CDCl₃) of S8.

label	macromonomer ^a	M_{n}^{b} (Da)	D^b
NB-oSty4	Disperse NB-oSty4	~630°	1.16 ^c
S2	Discrete NB-oSty2	460.26	1.00
S4	Discrete NB-oSty4	668.46	1.00
S6	Discrete NB-oSty6	876.49	1.00
S 8	Discrete NB-oSty8	1084.41	1.00

Table S1. Disperse and discrete macromonomers used in this study

^{*a*}The numbers represent the number of styrene repeat units. ^{*b*}Determined using MALDI-ToF. ^{*c*}Determined using SEC.



Figure S7. ¹H NMR (500 MHz, CDCl₃) of PBP-S2₂₂ and PBP-S2₃₆.



Figure S8. ¹H NMR (500 MHz, CDCl₃) and ¹³C NMR (125 MHz, CDCl₃) of PBP-S4₃₀.



Figure S9. ¹H NMR (500 MHz, CDCl₃) of PBP-S6₂₇.



Figure S10. ¹H NMR (500 MHz, CDCl₃) of PBP-S8₃₂.



Figure S11a. ¹H NMR (500 MHz, CDCl₃) of b-PBP-S2₂₀S8₁₀ (diblock A)



Figure S11b. ¹H NMR (500 MHz, CDCl₃) of b-PBP-S8₂₀S2₁₀ (diblock B).



Figure S12a. ¹H NMR (500 MHz, CDCl₃) of b-PBP-S8₅S2₂₀S8₅ (triblock A).



Figure S12b. ¹H NMR (500 MHz, CDCl₃) of b-PBP-S8₁₀S2₁₀S8₁₀ (triblock B).



Figure S12c. ¹H NMR (500 MHz, CDCl₃) of **b-PBP-S2₁₀S8₁₀S2₁₀** (triblock C).



Figure S13. SEC trace of disperse NB-oSty4 (black) and the isolated macromonomer libraries (S2–S8).



Figure S14. MALDI-ToF spectra of discrete macromonomers S3 (red), S4 (green), S5 (blue), S6 (purple), S7 (navy), and S8 (orange) after chromatographic separation of disperse NB-oSty6.



Figure S15. FTIR spectra of **NB-oSty4** (black), **S2** (brown), **S4** (green), and **S8** (orange). The intensity of the =C–H stretch ($3000 - 3100 \text{ cm}^{-1}$, inset) corresponding to the aromatic ring increases with the length of discrete macromonomers (S2, S4, and S8). The spectra were normalized using the vibrational frequency of the carbonyl group (C=O stretch, 1720 cm⁻¹).



Figure S16. FTIR spectra of PBP-S4 $_{30}$ (blue) and b-PBP-S2 $_{20}$ S8 $_{10}$ (brown).



Figure S17. SEC traces of PBP-S8, PBP-S6, PBP-S4, and PBP-S2 bottlebrush series.



Figure S18. SEC traces of diblock b-PBP-S2₂₀S8₁₀ and b-PBP-S8₂₀S2₁₀.



Figure S19. SEC traces of triblock b-PBP-S8₅S2₂₀S8₅ and b-PBP-S8₁₀S2₁₀S8₁₀.

Table S2. Bottlebrush polymers synthesized and used in this study

sample ^a	M_{n}^{b} (kDa)	D^b
PBP-S2 ₅	2.5	1.15
PBP-S2 ₁₃	6.0	1.08
PBP-S2 ₂₂	10.1	1.05
PBP-S2 ₃₆	16.8	1.04
PBP-S2 ₇₇	35.6	1.12
PBP-S2 ₁₈₀	82.8	1.03

A. Precision bottlebrush polymers (PBPs) - from S2

B. Precision bottlebrush polymers (PBPs) - from S4

sample ^a	$M_{\rm n}{}^b$ (kDa)	D^b
PBP-S4 ₅	3.2	1.12
PBP-S4 ₁₀	6.8	1.11
PBP-S4 ₃₀	20.2	1.08
PBP-S4 ₉₀	60.2	1.09

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sample ^a	M_{n}^{b} (kDa)	D^b
PBP-S6 ₄	3.2	1.11
PBP-S6 ₆	4.9	1.09
PBP-S6 ₁₄	12.3	1.06
PBP-S6 ₂₇	24.0	1.06
PBP-S6 ₈₃	72.7	1.13

D. Precision bottlebrush polymers (PBPs) - from S8

sample ^a	M_{n}^{b} (kDa)	D^b
PBP-S8 ₄	3.9	1.08
PBP-S888	8.5	1.05
PBP-S8 ₁₂	12.7	1.05
PBP-S8 ₃₂	34.5	1.11
PBP-S8 ₂₆₇	290	1.06

sample ^{<i>a</i>}	M_{n}^{b} (kDa)	D^b
b-PBP-S85S220S85	20.3	1.05
b-PBP-S2 ₁₀ S8 ₁₀ S2 ₁₀	21.8	1.05
b-PBP-S2 ₂₀ S8 ₁₀	16.1	1.08
b-PBP-S810S210S810	35.6	1.06
b-PBP-S820S210	28.7	1.09

E. Precision multiblock bottlebrush polymers (b-PBPs)

^aThe regular number represents $N_{\rm SC}$ and the subscripted number represents $N_{\rm BB}$. ^bMeasured using SEC-MALS



Figure S20. Glass transition temperature (T_g) of discrete macromonomers S2 - S8 (red). T_g of disperse NB-oSty₄ is shown in black.



Figure S21. DSC traces of PBP-S8, PBP-S6, PBP-S4, and PBP-S2 series.

Determining $N_{\rm BB}^*$ for PBP-S8, PBP-S6, PBP-S4, PBP-S2, and $N_{\rm SC}^*$

To determine the critical backbone length $N_{\rm BB}^{*}$ for each of the $N_{\rm SC}$, an exponential fitting

 $T_g = T_{g,\infty BB} - A * e^{-b(n-1)}$ was used on the plot of T_g as a function of N_{BB} (Figure 2b), similar to the fitting used in determining effective conjugation length of conjugated polymers,^{3,4} and $N_{BB}* = \frac{lnA}{b} + 1$. Similarly, to determine $N_{SC}*$, the same fitting was used on the plot of $T_{g,\infty}$ as a function of N_{SC} .



Figure S22. Exponential fitting to determine N_{BB}^* for PBP-S8, -S6, -S4, -S2, and N_{SC}^* .



Figure S23. DSC traces of PBP-S2₃₀ (blue), multiblocks b-PBP-S8₅S2₂₀S8₅, b-PBP-S2₁₀S8₁₀S2₁₀, b-PBP-S2₂₀S8₁₀, b-PBP-S2₂₀S8₁₀, b-PBP-S8₂₀S2₁₀ (black), and PBP-S8₃₀ (red).

entry	sample ^a	$M_{ m n,S2~(Da)}~(w_{ m S2})^b$	$M_{ m n,S8(Da)}(w_{ m S8})^b$	$T_{\rm g,S2(K)}{}^c$	$T_{\rm g,S8(K)}{}^c$	$T_{\rm g,Fox(K)}{}^d$	T _{g,Fox (•C)}
1	b-PBP-S85S220S85	9200 (0.46)	2* 5425 (0.54)	309	340	325	52
2	b-PBP-S2 ₁₀ S8 ₁₀ S2 ₁₀	2* 4600 (0.46)	10850 (0.54)	306	344	326	53
3	b-PBP-S2 ₂₀ S8 ₁₀	9200 (0.46)	10850 (0.54)	309	344	327	54
4	b-PBP-S810S210S810	4600 (0.17)	2* 10850 (0.83)	306	344	337	64
5	b-PBP-S820S210	4600 (0.17)	21700 (0.83)	306	345	338	64

Table S3. T_g prediction of multiblocks from Fox equation

^{*a*}The regular number represents N_{SC} and the subscripted number represents N_{BB} , entry 1,2, and 4 are triblock while entry 3 and 5 are diblock. ^{*b*} M_n of S2 or S8 block = $M_{n,macromonomer} \times N_{BB,block}$, weight fraction is shown in parenthesis. ^{*c*}Glass transition temperature of each block assuming it was a bottlebrush homopolymer, estimated from fitting on Figure 2c. ^{*d*}Predicted glass transition from Fox equation (Eq. S4)

GLASS TRANSITION BLENDING THEORIES

The Couchman equation is given by:

$$ln(T_g) = \frac{w_1 \Delta C_{p,1} ln(T_{g,1}) + w_2 \Delta C_{p,2} ln(T_{g,2})}{w_1 \Delta C_{p,1} + w_2 \Delta C_{p,2}}$$
(S1)

where w_i refers to weight fraction of the *ith* component, and $\Delta C_{p,i}$ refers to the difference in C_p in the glass and liquid states of the *ith* component. It is derived from the thermodynamic relationship between entropy and heat capacity:

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} C_p d \ln T$$
(S2)

combined with the idea that, at a second order transition, the entropies of each state must be equal. See reference^{5,6} for full derivation. By dividing the numerator and denominator by $\Delta C_{n,2}$ the Couchman equation yields:

$$ln(T_g) = \frac{w_1 \frac{\omega_{p,1}}{\Delta C_{p,2}} ln(T_{g,1}) + w_2 ln(T_{g,2})}{w_1 \frac{\Delta C_{p,1}}{\Delta C_{p,2}} + w_2}$$
(S3)

Using the pure T_g for **PBP-S2**₁₃ and **PBP-S8**₁₂, the blend T_g data in Figure 3c can be fit with fitting parameter $\Delta C_{p,1}/\Delta C_{p,2}$. Linear least squares regression to the data in Figure 3c (blends of **PBP-S2**₁₃ and **PBP-S8**₁₂) yields $\Delta C_{p,1}/\Delta C_{p,2} = 0.84$. From the DSC data in Figure 3b, $\Delta C_{p,S8,12} = 0.22$ and $\Delta C_{p,S2,13} = 0.28$, yielding $\Delta C_{p,S8,12}/\Delta C_{p,S2,13} = 0.79$, a good match for the fit, which yields 0.84.

The Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$
(S4)

was developed by Fox in 1956. The Fox equation results from the Couchman equation if it is assumed that $\Delta C_{p,1}T_{g,1} \approx \Delta C_{p,2}T_{g,2}$, and if the T_g 's are not very different. Because it does not require estimates of ΔC_p , the Fox equation is commonly used to predict the T_g in polymer blends and statistical copolymers. Since DSC data is available in this case, the Couchman equation provides a more accurate prediction.

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