Programming the Properties of Branched Polymers Through Precision Architectures

Michael R. Dearman
Louisiana State University and Agricultural and Mechanical College

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PROGRAMMING THE PROPERTIES OF BRANCHED POLYMERS THROUGH PRECISION ARCHITECTURES

A Thesis

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in

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by

Michael R. Dearman
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Abstract

The glass transition of branched polymers is determined by multiple structural parameters that dictate their inter- and intramolecular interactions, and ultimately, their molecular packing in the amorphous phase. Here we examined the impact of side chain length, backbone length, molecular weight composition, and topology on the glass transition behavior of bottlebrush polymers. Through examining precision bottlebrush polymer libraries (PBP, $D_{SC} = 1.0$), we find the infinite molecular weight $T_g$ is reached at a specific brush length after which the effect of the side-chain length dominates. Being a factor more dominant than the backbone, side-chain length affects the $T_g$ of bottlebrush polymers across all sizes and topology variations. To demonstrate the versatility of side chain engineering strategies, a broad range of $T_g$ and glass transition behavior was targeted through judicious choice of side chain length, blend ratios, and brush topology. PBPs yield precise $T_g$ with some values only accessible through making PBP blends at the cost of $T_g$ broadening. Ultimately, multiblock PBPs combine the best features of both approaches; the ability to target arbitrary $T_g$ while maintaining sharp glass transition.
Chapter 1. Introduction

Polymers are unique, versatile materials composed of simplistic repeating monomer units. Because of this unique composition, natural polymers like cellulose, collagen, DNA, and RNA are widespread building blocks in biology. In fact, these natural biopolymers perpetuate the existence of all life, fulfill diverse functionalities, and respond to a large number of external stimuli. Biopolymers that store and transfer information like DNA and RNA also have well-defined sequence and tacticity. Further, these biopolymers are naturally discrete, having only a single length of polymer chain with well-defined properties and applications. From these attributes, a class of polymers called precision polymers can be defined, composed mainly of biopolymers but also a growing number of synthetic polymers. In contrast to biopolymers, most synthetic polymers have simplistic sequences and properties. For this reason, research interest in developing synthetic polymers with discrete molecular weight distributions, precise sequences, and well-defined structure-properties has grown significantly. However, this level of precision is largely limited to linear polymers.

In the regime of branched polymers, only dendrimers have achieved a similar level of control as their linear counterparts. Unfortunately, they are limited in scope by their exhaustive synthetic strategies. By contrast, branched polymers like bottlebrush polymers have robust synthetic strategies known as grafting-from, grafting-to, and grafting-through, which produce polymers with side chains densely grafted to a linear backbone.

However, the structural complexity of bottlebrush polymers, coupled with their lack of precision in synthesis relative to dendrimers, is accompanied by an exponential increase in structural variation and inherent loss of control, specifically with respect to the uniformity of the bottlebrush side chains. Because of these characteristics, soft matter like bottlebrush polymers
have largely not achieved the same level of precision as their linear or dendrimer counterparts. Addressing this structural precision challenge by limiting dispersity will narrow the gap between real-world materials and their theoretical models, ultimately improving our understanding of their structure-property relationships.

Controlling dispersity is paramount for elucidating structure-property relationships. A small variation in dispersity has a significant impact on the optoelectronic, NMR dynamics, and self-assembly behaviors of linear oligomers and polymers. Consistent and precise phase separation behaviors were also reported for block copolymers having discrete blocks. The growing importance of suppressing structural heterogeneity for understanding the fundamental properties of brush polymers was also demonstrated in recent reports on precision bottlebrush polymers (PBP, $D_{\text{side chain}} = 1.0$); By controlling the dispersity of the bottlebrush side chains and ultimately, the precision of their architecture, we have programmed bottlebrush polymer properties such as phase behavior at the air-water interface and glass transition temperature.

1.1. Controlling dispersity

To tackle the issue of polymer dispersity, derivative radical polymerization methods with narrow molecular weight distributions like atom transfer radical polymerization (ATRP) were developed with pseudo-“living” reaction mechanisms. The reaction mechanism of this polymerization method produces an activation-deactivation equilibrium that reduces the total number of free radicals in the system, suppressing termination (Figure 1.1).
Figure 1.1. Reaction mechanism of ATRP. The ATRP rate constant that governs the activation-deactivation equilibrium, $k_{atp}$, is defined as $k_{act}/k_{deact}$.

This polymerization method is referred to as controlled radical polymerization because of the narrow molecular weight distribution it produces (Figure 1.2).
The narrower molecular weight distribution provides relatively consistent properties. However, values of dispersity from this approach are typically around $D = 1.1$, approaching but not quite achieving discrete materials.

To synthesize inherently discrete materials, step-wise deprotection and coupling reactions are utilized to couple monomers and then entire chains, discretely. Takizawa et al. used this approach to synthesize well-defined caprolactone oligomers. First, $\varepsilon$-caprolactone ring opening produced the starting monomer. Following ring opening, the material was split, and the $\alpha$-chain ends (hydroxyl group) of one set and the $\omega$-chain ends (carboxyl chain-end) of the other set were reacted with protecting groups $t$-butyldimethylsilyl (TBDMS) ether and benzyl (Bn) ester, respectively (Figure 1.3).
Following protection, esterification of monomer units 2 and 3 produces discrete dimer. However, this dimer retains its terminal protecting groups, preventing further reaction. To continue the coupling steps, the material must be split, and the $\alpha$- and $\omega$- chain ends selectively deprotected in separate reactions, allowing the esterification of two dimer units to produce discrete 4-mer. The TBDMS chain end can be deprotected back to a hydroxyl group using tetra-n-butyl ammonium fluoride (TBAF). Meanwhile, the Bn chain end was deprotected into a carboxyl group through hydrogenation catalyzed by palladium on carbon (Pd/C). Ultimately, these steps can be continued iteratively to yield discrete oligomers with larger degrees of polymerization (Figure 1.4).
Figure 1.4. Sequential deprotection and esterification of caprolactone oligomers to yield discrete materials.

SEC was used to confirm production of discrete caprolactone oligomers from this coupling strategy (Figure 1.5).
Figure 1.5. SEC traces for oligo(caprolactone) dimer to 64-mer.¹⁹

In general, this approach affords polymers with > 95% purity with only small amounts of unconverted lower molecular weight oligomers as impurities.

Unfortunately, this type of step-wise synthesis is exhaustive and impractical for large-scale production of discrete materials. Recognizing this problem, Lawrence et al. utilized ATRP to produce narrow disperse tert-butyl acrylate (TBA) oligomers, as mentioned previously.²⁰ Following synthesis, large-scale (15 g) flash chromatographic separation isolated discrete materials with high yield (Figure 1.6).

![Figure 1.6. MALDI-ToF of separated discrete materials from automated column chromatography.²⁰](image)

These discrete chains can be used as precursors for other materials by converting the terminal bromine chain end into functional groups. As an example, bromine terminated oligomers
can be easily converted to norbornenyl-terminated oligomers and polymerized into bottlebrush polymers with well-defined side chains using *grafting-through* ring opening metathesis polymerization (ROMP). By extending this precision to branched polymers, we hypothesized we could tune properties such as glass transition temperature.

Hawker, Whittaker, and coworkers have utilized separation to produce discrete materials with well-defined ¹⁹F NMR dynamics. Firstly, they synthesized trifluorethane-terminated (CF₃) oligo(TBA) from RAFT. Utilizing automated separation, they obtained discrete oligo(TBA)-CF₃. The CTA of these discrete materials was cleaved, and the tert-butyl groups were deprotected to afford water-soluble oligo(AA)-CF₃.

![Figure 1.7. Synthesis of discrete oligo(AA)-CF₃.](image)

Following synthesis of these discrete materials, the ¹⁹F NMR was analyzed, revealing the discrete materials had much sharper signal compared to the disperse material. Further, diffusion coefficients were used to identify the species within the disperse material.
Hawker and coworkers have also utilized chromatographic fractionation to produce well-defined libraries of ABC triblock polymers. They synthesized ABC and ACB triblock terpolymers with poly(4-methyl caprolactone), poly(dodecyl acrylate), and poly(2,2,2-trifluorethyl acrylate) blocks through sequential ROP and ATRP.

Figure 1.9. Synthesis of ABC and ACB triblock terpolymer disperse materials.
Following synthesis, they utilized chromatographic fractionation to obtain well-defined libraries of triblock polymers. These triblock polymer libraries were analyzed using SAXS to obtain their composition profile.

![Diagram](image)

Figure 1.10. (a) Composition of five parent materials and (b) Library of 87 well-defined, fractionated ABC triblock terpolymers generated via automated chromatography.  

Hawker and coworkers have also analyzed the effect of branching for discrete PEG-based drug delivery agents. Traditional DMG-PEG2000, the delivery agent used in the Moderna COVID-19 vaccine, elicits an immune response from PEG antibodies present in the human body. These anti-PEG antibodies have increased in the population from 0.2% in 1980 to 72% in 2016. Further, traditional DMG-PEG2000 is disperse, making it vulnerable to batch-to-batch variation. For the synthesis of this branched PEG, a 1,2-DMG initiator was used to polymerize PEG acrylate via ATRP.
Figure 1.11. Synthesis of disperse branched PEG amphiphiles.

Following synthesis, the PEG amphiphiles were separated into discrete species using automated column chromatography. They found discrete branched PEG-based drug delivery agents elicited a markedly lower anti-PEG antibody response.

Figure 1.12. Protein binding studies. a) Schematic illustration of SPR measurements. b) BSA and anti-PEG antibody binding measured through SPR experiments.
Chapter 2. Experimental

2.1. 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 F254 TLC plates from EMD Millipore and visualized using 254 nm UV, bromocresol green, or potassium permanganate. Automated flash chromatography of oligomers and macromonomers was performed with a Biotage Isolera One unit equipped with an evaporative light scattering detector (ELSD, Teledyne ISCO), Biotage KP-SIL SNAP/SNAP Ultra cartridge series (25 g/50 g/340 g), and a hexane/ethyl acetate gradient. High resolution polymer purifications were performed using preparative-scale recycling size exclusion chromatography (rSEC, LaboACE LC-5060) equipped with a cross-linked polystyrene/divinylbenzene column (PS/DVB, JAIGEL series) eluting with chloroform.

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 (λ = 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. \(^1\)H and \(^{13}\)C 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 (NaTFA) 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. 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.
2.2. Synthesis of oligo(styrene) using ATRP

To an oven dried 40 mL vial, copper(I)bromide (CuBr) (0.5 equiv.), N,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).

2.3. Synthesis of ω-hydroxyl-terminated oligo(styrene)

To an oven dried 40 mL vial, silver perchlorate (815 mg, 3.94 mmol) was added and degassed for 20 min. Oligo(styrene) (2000 mg, 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. 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).

2.4. Synthesis of ω-norbornenyl oligo(styrene) macromonomer

\[ \text{Disperse NB-oSty4} \]

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).
2.5. Synthesis of bottlebrush homopolymers

Grubbs 3<sup>rd</sup> generation catalyst (G3) was prepared following reported procedures, 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<sup>rd</sup> generation catalyst (IMesH)<sub>2</sub>(Cl)<sub>2</sub>(C₅H₅N)<sub>2</sub>Ru=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).

2.6. Synthesis of multiblock bottlebrush polymers
Triblock b-PBP-S₈.S₂.S₈.

Grubbs 3rd generation catalyst (G3) was prepared following reported procedures, 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. 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).
Chapter 3. Versatile strategies to tailor glass transition temperatures of bottlebrush polymers

Glass transition is an amorphous solid-viscous liquid transition of polymers. This transition provides valuable insights into the temperature-dependent dynamics of polymer chains.\textsuperscript{25} Often, the temperature range where polymers undergo this transition ($T_g$) determines their end use and performance.\textsuperscript{26,28} To tune the $T_g$ of polymers, synthetic and practical strategies were developed to tailor chain length, backbone and side-chain chemistry, and blend composition.\textsuperscript{29–33} Despite such advances,\textsuperscript{20,34,35} understanding the effect of structure on $T_g$ has remained a grand challenge for linear polymers\textsuperscript{36,37} and a grander one for non-linear architectures due to a combination of side-chain and backbone dispersities.\textsuperscript{35,36,38–41}

Precision bottlebrush polymers (PBP) and multiblock PBPs (b-PBP) are promising platforms for addressing this grand challenge of designing novel soft materials and additives with predictable and accurate glass transition behavior. Specifically, the synthesis of PBP and b-PBP libraries via grafting through ring opening metathesis polymerization (ROMP) of discrete macromonomers opens a pathway for investigating the impact of side-chain, backbone, blend composition, and polymer topology on glass transition. PBPs have the unique feature of uniform backbone stiffness along the polymer length, allowing segmental chain dynamics and brush-brush interactions to be studies with exceptional consistency and accuracy.\textsuperscript{42} We posit the $T_g$ of tailored bottlebrush polymers could be accurately predicted through precisely controlling bottlebrush dimension, blend composition, and block topology without changing their chemical makeup (Scheme 3.1). This level of design is in stark contrast with commonly adopted small molecule additive-based strategies that pose a range of reliability and environmental issues. Our findings reveal three fundamental insights: (1) the $T_g$ is a function of side-chain ($N_{SC}$) and backbone length
(N_{BB}) up to a critical backbone length (N_{BB}^*) , after which it is only a function of N_{sc}; (2) a theoretically accurate and broad range of T_g can be accessed through precise artificial binary blends; (3) N_{BB}^* values and T_g-weight fraction correlations enable de novo design of multiblock bottlebrushes with accurate and precise T_g.

Scheme 3.1. Structural heterogeneity imposes significant challenges for designing bottlebrush polymers with targeted properties. This study: strategies for elucidating factors that impact the T_g of bottlebrush polymers and enable de novo design of precision bottlebrush polymers with targeted T_g.

**Synthesis of macromonomers and precision bottlebrush polymers** Macromonomers were synthesized through a combination of controlled polymerization techniques and chain-end functionalizations. Styrene oligomers were first prepared via atom transfer radical polymerization (ATRP) followed by bromine chain end conversion to yield ω-hydroxyl oligo(styrene). As an added advantage to this strategy, traces of non-functional oligomers and other byproducts are easily removed using a plug column to afford synthetically pure OH-terminated oligostyrenes, as confirmed through NMR, SEC, and TLC analysis. Subsequent esterification with exo-5-norbornene carboxylic acid yielded the targeted product, ω-norbornenyl oligo(styrene) (NB-oSty) macromonomers (M_n, SEC = 600 Da, D = 1.2). Finally, the disperse macromonomers were
subjected to flash column chromatography and/or high resolution recycling size exclusion chromatography (rSEC) to isolate a series of discrete macromonomers. Here the terms S2, S4, S6, and S8 are used to indicate discrete dimer, tetramer, hexamer, and octamer macromonomers, respectively. The structural purity of discrete macromonomers were confirmed using NMR, SEC, and MALDI-ToF analysis ([S4+Na]: calc.= 691.38, found = 691.45, [S6+Na]: calc.= 899.50, found = 899.48, [S8+Na]: calc.= 1107.64 , found = 1107.41 , Figure 3.1).

Figure 3.1. 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.

With discrete macromonomer libraries in hand, PBPs with various $N_{\text{sc}}$ and $N_{\text{bb}}$, including multiblock-PBPs, were synthesized via grafting-through ring opening metathesis polymerization (ROMP, Figure 3.2a). Owing to the versatility of ROMP, all polymer samples were narrow disperse ($D_{\text{sc}} < 1.2$), as seen in their SEC-MALS chromatograms (Figure 3.3). $^1$H NMR analysis
of PBP samples provides insights on the structural changes as \( N_{sc} \) increases. The broadness and relative intensity of the aromatic protons with respect to the backbone olefinic protons (4.8-5.5 ppm) increases with \( N_{sc} \), and the integration ratio reflects the number of styrene units per side chain (Figure 3.2b). The sharpness of the signal at 2.8 ppm decreases as \( N_{sc} \) increases from 2 to 8, characteristic of the side chain progression from a small molecule- to a polymer. For the triblock structure, 1H NMR analysis shows the broadening of the aromatic proton signals with increasing S8 content from b-PBP-S8\(_{S2}\) to b-PBP-S8\(_{n}\)S2\(_{m}\), the integration ratio of the olefinic protons to the aromatic protons highlights the average number of styrene units per side chain. Overall, the ratio of S8 to S2 content is reflected in the spectra for both triblock structures as b-PBP-S8\(_{S2}\) compares to PBP-S2 and b-PBP-S8\(_{n}\)S2\(_{m}\) compares to PBP-S8.
Figure 3.2. (a) Synthesis of topologically uniform and multiblock precision bottlebrush polymers via grafting-through ROMP. (b) $^1$H NMR spectra of homobrush $\text{PBP-S}_{84}$ (blue), homobrush $\text{PBP-S}_{66}$ (red), triblock $b$-$\text{PBP-S}_{84}$-$\text{S}_{84}$ (light purple), and triblock $b$-$\text{PBP-S}_{84}$-$\text{S}_{84}$-$\text{S}_{84}$ (dark purple). All spectra are normalized to the resonance of the methylene proton adjacent to the side chain end ($d$, 3.8 ppm). Integrations of the peaks are shown in italics.

Figure 3.3. SEC traces of $\text{PBP-S}_{84}$, $\text{PBP-S}_{66}$, $\text{PBP-S}_{44}$, and $\text{PBP-S}_{22}$ bottlebrush series.

The impact of side chains and backbone on $T_c$. Differential scanning calorimetry (DSC) analysis showed that both discrete macromonomers and precision bottlebrush polymers exhibit size-dependent glass transition behaviors (Figure 3.4-3.5). The $T_c$ of $S_{22}$, $S_{44}$, $S_{66}$, and $S_{84}$ are $-21.7$, $-24.3$, $-27.3$, and $-29.8$, respectively.
-6.9, 15.4, and 35.8 °C, respectively, in agreement with prior reports.\textsuperscript{20,29,30} Importantly, this result provided the mission to focus on PBPs because they are less impacted by structural heterogeneity and batch-to-batch variation.

Figure 3.4. Glass transition temperature ($T_g$) of discrete macromonomers S2 - S8 (red). $T_g$ of disperse NB-oSty4 is shown in black.
Figure 3.5. DSC traces of PBP-S2, PBP-S4, PBP-S6, and PBP-S8 series.

Glass transition studies of PBP samples with systematically varied side-chain and backbone length showed their $T_g$ is impacted more by side-chain ($N_{SC}$) than backbone length ($N_{BB}$). For all PBP samples, regardless of side-chain length, $T_g$ increases with increasing $N_{bb}$ until a critical backbone length ($N_{bb}^*$) is reached (Figure 3.6a, b). Beyond $N_{bb}^*$, the $T_g$ of PBP approaches an asymptotic value, the glass transition temperature at infinite molecular weight ($T_{g,\infty}$, Figure 3.6c). Using
exponential fitting similar to the fitting for effective conjugation length of conjugated polymers \( (T_g = T_g,_{\infty} - A^*e^{-b(n-1)}) \) and plotting \( T_g \) as a function of \( 1/N_m \) (Flory-Fox eq., \( T_g = T_g,_{\infty} - K/N_m \)), the \( T_g,_{\infty} \) for PBP-S2, -S4, -S6, -S8 were estimated to be 40, 60, 69, and 75 °C, respectively. Using the same fitting approach and the equation for effective conjugation length \( (N_m^* = \ln(A)/b + 1) \), the \( N_m^* \) for PBP-S2, -S4, -S6, -S8 were estimated to be 50, 21, 15, and 10, respectively (Figure 3.7). When plotted (Figure 3.6d), this data implies an \( N_m^* \), which was calculated to be 19 when fit with a similar exponential fitting.

![Figure 3.6](image)

Figure 3.6. (a) Schematic showing \( T_g \) dependence on \( N_{BB} \) and \( N_{SC} \). (b) Glass transition temperature of PBP-S2 (blue diamond), PBP-S4 (green triangle), PBP-S6 (purple circle), and PBP-S8 (red square) libraries. (c) Linear Flory-Fox plots of bottlebrush series. (d) \( T_g,_{\infty} \) with varied side chain length.
Figure 3.7. Exponential fitting to determine $N_{nn}^*$ for PBP-S2, -S4, -S6, and -S8.

Our results show $N_{nn}^*$ is inversely related to $N_{sc}$ such that $T_{g,\infty}^{BB}$ is approached as the total degree of polymerization ($N = N_{nn}^* \times N_{sc}$) reaches 80-100 styrene units, regardless of PBP configuration. As the side-chain length increases, the corresponding $N_{nn}^*$ decreases exponentially (Figure 3.6c). The importance of side chain dispersity is reinforced by the fact that, despite the small $N_{sc}$ values, our finding are consistent with the well-documented total N of 90-100 for brush-shaped ($T_{g,\infty} = 95$ °C) and linear polystyrenes ($T_{g,\infty} = 100$ °C). As mentioned previously, the $T_{g,\infty}^{BB}$ values obtained from calculating $N_{nn}^*$ for each PBP can be correlated with their respective $N_{sc}$ to determine the critical side chain length, $N_{sc}^*$. The identification of $N_{sc}^*$ for $N_{nn} > N_{nn}^*$ provides the insight on the maximum $T_{g}(T_{g,\infty})$ of PBP. Using a similar fitting approach, the $N_{sc}^*$ for styrenic
PBP was estimated to be ~19, and its \( T_{g,\infty} \approx 85 \text{ °C} \) (Figure 3.6d). We confirmed the fitting accuracy by calculating the \( T_g \) of PBP-S10 \( (T_{g,\text{calc}} = 78.5 \text{ °C}) \) and finding its difference with experimental data to be negligible (PBP-S10, \( T_{g,\text{exp}} = 78 \text{ °C} \)).

The ability to access a targeted \( T_g \) solely through varying \( N_{sc} \) with negligible impact from backbone parameters (at \( N_{sa} > N_{sa}^* \)) is significant. Existing strategies to tailor \( T_g \) by changing overall \( M \) and/or \( D \) are limited by lack of range and precision, with significant concerns about reproducibility and detrimental changes to physical properties. The uniform topology of PBPs and the identification of \( N_{sa}^* \) and \( N_{sa}^* \) open an unprecedented access to a wide variety of styrenic bottlebrush polymers with a broad range of molecular weight and independently tailorable glass transition temperature.

**The impact of composition on \( T_g \)** Artificial blends of precision polymers offer a significant promise for preparing multifunctional materials with precisely tunable properties.\(^{12,46-48}\) To address the gaps between unique \( T_{g,\infty} \) at different \( N_{sc} \), we hypothesized that a binary blend of PBP can be prepared to afford a chemically homogeneous mixture with its \( T_g \) located between the unique \( T_{g,\infty} \) of each component. To test this hypothesis, we examined the \( T_g \) of PBP-S2, \( (A, T_{g,\infty} = 35 \text{ °C}), \) PBP-S8, \( (B, T_{g,\infty} = 74 \text{ °C}) \) and their artificial blends (4 samples, \( w_A: w_B = 3:1, 2:1, 1:1, 1:3, \) respectively, Figure 3.8a). Each PBP blend exhibits a single compositional dependent \( T_g \) and a broader glass transition profile when compared with those of the pure components. This trend is consistent with previous studies and confirmed that each blend is chemically homogenous and completely miscible (Figure 3.8b).\(^{49}\)

**Couchman-Karasz and Fox equations** Further analysis showed that the \( T_g \) of artificial blends fit reasonably well with the calculated values using Fox\(^{50}(\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}})\) and Couchman–
Karasz equations \( \ln(T_g) = \frac{w_1 \Delta C_{p,1} \ln(T_{g,1}) + w_2 \Delta C_{p,2} \ln(T_{g,2})}{w_1 \Delta C_{p,1} + w_2 \Delta C_{p,2}} \).\textsuperscript{31} Despite its simplicity, the empirical Fox equation only considers the inverse \( T_i \) of a blend as the mass fraction weighted sum of the inverse pure component \( T_i \) values. In contrast, the Couchman–Karasz equation follows a classical thermodynamic viewpoint, where the blend \( T_i \) is defined by the requirement that the system entropy for the glassy state is identical to that for the rubbery state, and entropy is calculated using the integral of \( C_p/T \).\textsuperscript{51,52} In comparing the fitness of the \( T_i \) data with both models (Figure 3.8c), the Couchman–Karasz model fits our data slightly better (\( R^2 = 0.997 \) (C–K) vs. 0.993 (Fox)). The near-ideal agreement between both theoretical models and experimental data is attributed to the chemical homogeneity of PBP blends; a larger discrepancy between calculations (especially the Fox model) and experimental data is generally expected for heterogeneous or partially miscible blends.

The Fox equation can be easily derived from the Couchman-Karasz equation following a few minor assumptions. If \( T_{i1}/T_{i2} \) is not greatly different from 1, the Couchman-Karasz equation simplifies to \[ T_g = \frac{w_1 \Delta C_{p,1} T_{g,1} + w_2 \Delta C_{p,2} T_{g,2}}{w_1 \Delta C_{p,1} + w_2 \Delta C_{p,2}}, \] which is similar to the Wood equation. By assuming \( C_p, i T_g, i = \text{constant} \), the familiar Fox equation can be derived: \[ \frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}. \]

Due to sample homogeneity, the \( T_i \)-composition plot (Figure 3.8) shows that even if the \( T_i \) of one pure component is offset by a few degrees (e.g., when \( N_{ni,1} < N_{ni,1}^* \)), the accuracy of \( T_i \) prediction is still within the experimental uncertainty of \( T_i \) measurements, as long as the backbone length of the other component is equal to or greater than its critical length (\( N_{ni,2} \geq N_{ni,2}^* \)). This insight, together with the reasonable precision offered by the Fox and C–K models, prompted us to examine in detail the impact of topology on \( T_i \).
The impact of brush topology on $T_g$  Having established the importance of $N_{BB,*}$ and the $T_g$–weight fraction correlation for PBP mixtures, we hypothesized that the glass transition of a uniform multiblock bottlebrush polymer (single component) can be targeted through designing their block parameter, sequence, and the knowledge of the pure components ($N_{BB,i,*}$, thermophysical properties). There are two reasons that support this hypothesis. (i) When $N_{BB} > N_{BB,*}$, the block ‘junction’ has a negligible impact on $T_g$. Using PBP-S8$_{20}$ as an example, the sample $T_g$ (~74 °C) does not change when the brush is ‘cut’ into two PBP-S8$_{10}$ brushes ($N_{BB} \geq N_{BB,*}$ of 10). However significant $T_g$ decrease is observed when PBP-S8$_{20}$ is ‘cut’ equally into four PBP-S8$_{5}$ brushes ($T_g = 65 \ ^\circ C, N_{BB} < N_{BB,*}$). (ii) Following (i), for two-component multiblock PBP, when the backbone length of the block with longer $N_{BB}$ exceeds its critical $N_{BB,*}$, its $T_g$ can be estimated with sufficient precision using binary blend models (Fox or C–K equations).
To test this hypothesis, we prepared a total of seven PBP and block-PBP samples (a – g, Figure 3.9). As the sample series transitioned from PBP-S8\textsubscript{30} (a) to PBP-S2\textsubscript{30} (g), S8 fraction was gradually decreased and its block rearranged to examine the impact of block size and sequence. Sample b (diblock) and c (triblock) are block-PBP isomers with an average \( N_{sc} \) of 6. Sample d (diblock), e (triblock), and f (triblock) are block-PBP isomers with an average \( N_{sc} \) of 4. Compositionally identical diblock and triblock PBPs with similar \( M_n \) were previously shown to exhibit topology-dependent packing at the air-water interface.\(^a\)

<table>
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<th>PBP</th>
<th>S8\textsubscript{30}</th>
<th>S2\textsubscript{10}S8\textsubscript{20}</th>
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<td>6</td>
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<tr>
<td>( T_g, \text{expt.} ) (°C)</td>
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<td>63</td>
<td>65</td>
<td>55</td>
<td>54</td>
<td>50</td>
<td>37</td>
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<tr>
<td>( T_g, \text{Fox ec.} ) (°C)</td>
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<td>64</td>
<td>64</td>
<td>54</td>
<td>53</td>
<td>52</td>
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</table>

Figure 3.9. (a) Experimental and predicted \( T_g \) data of multiblock isomers as the bottlebrush topology gradually transitions from PBP-S8\textsubscript{30} to PBP-S2\textsubscript{30}. Red arrow indicates block replacement of S8 with S2. Blue arrow indicates block rearrangement. (b) DSC traces of artificial blends of PBP-S8\textsubscript{30} and PBP-S2\textsubscript{30} vs triblock b-PBP-S8\textsubscript{8}S2\textsubscript{20}S8\textsubscript{8}.

As one-third of the S8 block in PBP-S8\textsubscript{30} is replaced by S2 in the diblock b and triblock c, their \( T_g \) decreases to 63–65 °C. This finding is consistent with the value predicted from Fox and C–K equations (Figure 3.9a), because the weight fraction of S8 for both samples are relatively high (82%). Furthermore, the \( T_g \) values for both isomers are similar because the block length of S8 is \( \sim 10 \) (\( \geq N_{BB,\text{PBP-S8}} \)). A similar trend can be seen for diblock d and triblock e. With a structure that resembles sample c having one of its S8 blocks at brush-end replaced with an S2 block, sample d
has a lower $T_g$ of 55 °C, and rearranging the block sequence of S8 to the center of the brush does not affect its $T_g$. However a further $T_g$ decrease of 5 °C was observed when the S8 block was split below $N_{\text{BB,S8}}$ and placed at both brush-ends. Once again, the binary blend-based theoretical models predicted their $T_g$ relatively well, with the qualitative trend of $T_g$ decrease for sample e and f being attributed to shorter S2 and S8 blocks, respectively.

We note that the deviation from experimental data is expected because the model does not fully capture the impact of block junctions when the length of one block is less than its $N_{\text{sc}}$, though this effect appears to be somewhat insignificant. The deviation seems to be mitigated by the fact that $N_{\text{sc}}$ is inversely proportional to $N_{\text{sc}}$ and the necessarily higher weight fraction for the block with longer $N_{\text{sc}}$. In other words, the longer $N_{\text{sc}}$ block reaches or exceeds $N_{\text{sc}}$ more readily, and contributes more weight fraction to the system.

The thermophysical property of multiblock PBP combines the accuracy of discrete side-chain topology and the precisely tailorable range of artificial blends. When compared with the broad glass transition behavior of artificial blends, all multiblock samples exhibit sharp glass transition behaviors similar to PBP. (Figure 3.9b), confirming the importance of discrete and designer topology for de novo design of bottlebrush polymers.
Chapter 4. Conclusions and Future Work

In summary, we reported the importance of structurally discrete side chains as a critical parameter for regulating the $T_g$ of bottlebrush polymers. We examined three approaches: tailoring the length of discrete side-chains ($N_{SC}$), tuning the composition of artificial blends, and designing brush topology. In the first approach we found $T_g$ to be more affected by side chain length than the backbone length ($N_{BB}$). When $N_{BB}$ is equal or longer than the critical backbone length ($N_{BB}^*$), the $T_g$ of bottlebrush polymers is independent of backbone length and dispersity. The second approach demonstrated that any $T_g$ value between the $T_g$ of two bottlebrush polymers can be precisely targeted through preparing artificial blends. The $T_g$ of polystyrene bottlebrushes can be tailored precisely from 25 °C to 78 °C without changing its chemical make-up.

Confirming this $N_{BB}^*$-dependent phenomena, the last approach combined the knowledge of $T_g$ as a function of $N_{BB}$, $N_{SC}$, and weight fractions, to enable the design of uniform multiblock bottlebrush polymers with tailorable well-defined thermophysical properties. The ability to maintain, tailor, or dramatically change the thermophysical properties of branched polymers through a combination of the strategies described above should prove useful for eliminating the commonly found structure–property–composition tradeoffs in a diverse range of fundamental studies and technological applications.

In the future, applying this method to other polymer families would provide a methodology to lower the $T_g$ of difficult to process polymers like PEEK. Enhancing the processability of these difficult polymers would open their applicability to a broad range of situations, in contrast to the limited use they see today.
References


Vita

Michael Dearman was born in Baton Rouge, Louisiana. He graduated from Louisiana State University with a B.S. in Chemical Engineering in May 2020. In August 2020, he became a graduate student at Louisiana State University and plans to receive his M.S. in Chemical Engineering in May 2023.