Synthesis of bottlebrush copolymers based on poly(dimethylsiloxane) for surface active additives

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ABSTRACT. Bottlebrush polymers have been used as surface-active additives for chemically-identical linear polymers because they spontaneously accumulate at surfaces through an entropy-

mediated process. In this work, we design functional bottlebrush polymer additives with mixed side-chain chemistries that can deliver unique surface properties. Bottlebrush polymers with poly(dimethylsiloxane) (PDMS) side-chains and bottlebrush copolymers with PDMS and poly(lactic acid) (PLA) side-chains are synthesized using ring opening metathesis polymerization. Contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and microscopy demonstrate a spontaneous accumulation of these additives at the film surface without lateral phase segregation. Bottlebrush polymers were found to enrich the film surface more strongly than linear block copolymers of PDMS-*b*-PLA, and the surface contact angle was tunable by varying the composition and quantity of added bottlebrush copolymer. Significantly, bottlebrush additives segregate rapidly, during film casting. This work demonstrates that low-surface energy bottlebrush copolymer additives can be used to introduce new surface properties in polymer films.

Introduction

Bottlebrush polymers have unique properties stemming from their highly branched architecture. The properties and target applications of bottlebrushes are primarily determined by the composition of the side-chain polymers, as they shield the backbone and are generally flexible and able to interact with their environment. Bottlebrush polymer macromolecules range in size from tens to hundreds of nanometers, may be spherical or elongated in shape,¹ and can be designed for applications including stimuli responsive films,² nanolithography,³ drug delivery,⁴⁻⁶ and lubricants,⁷⁻⁹ as discussed in a recent review.¹⁰

A potential application of bottlebrush polymers is as specialty additives to modify polymer film surface properties. Prior experimental¹¹⁻¹² and computational studies¹²⁻¹⁴ have demonstrated the surface segregation of branched polymers in blends with chemically identical

linear polymers. The migration of linear copolymer additives, where the additive contained a compatibilizing (same composition as matrix polymer) and low-surface energy component, has also been reported.¹⁵⁻¹⁸ In a recent study focusing on blends of bottlebrush and linear polystyrene (1:9 vol/vol), we found that bottlebrush polystyrene preferentially accumulated at air and substrate interfaces after thermal annealing. The bottlebrush side-chain composition matched that of the linear polymer matrix, and therefore segregation was driven by entropic effects.^{11, 14, 19} Here, we explore blends of bottlebrush copolymers that contain two different types of side chains (see Figure 1). The use of bottlebrush copolymers with two different side-chains introduces enthalpic interactions²⁰ as a driving force for segregation while simultaneously delivering a desired surface functionality.

Figure 1: Schematic for the modification of polymer thin films through the addition of bottlebrush copolymers, which segregate to the film surface due to enthalpic and entropic effects.

We focus on bottlebrush polymers and copolymers with poly(dimethylsiloxane) (PDMS) side-chains. PDMS is an inorganic polymer with low surface energy (~ 20 mN/m) and low glass transition temperature ($T_g \sim -120^\circ\text{C}$). PDMS has been demonstrated for applications including anti-biofouling,²¹⁻²⁶ directed self-assembly,²⁷⁻²⁸ nanolithography,^{3, 27-29} and gas separation membranes.³⁰⁻³¹ There are limited reports on branched PDMS polymers.³⁰⁻³⁶ RAFT polymerization of methacrylate-terminated PDMS has produced bottlebrush PDMS with side-

chain M_n of 1 or 4.3 kg/mol and backbone degree of polymerizations (DP) up to 70 for the shorter side-chains.³²⁻³³ Masuda et al³⁴ reported branched PDMS material with M_w up to 349 kg/mol but with broad molecular weight dispersity ($\mathcal{D} = 1.7 - 3.2$). An approach based on ring-opening metathesis polymerization (ROMP) was limited to very short oligo-PDMS chains, with a maximum side-chain DP of 8.³¹

Herein, we report the synthesis of bottlebrush polymers with PDMS side-chains and bottlebrush copolymers with PDMS and poly(lactic acid) (PLA) side-chains using a ROMP grafting-through synthesis approach and their use as surface-active additives. ROMP produces branched PDMS polymers and copolymers with a high grafting density and longer side-chains compared with previous synthetic approaches. To investigate the segregation of PDMS/PLA bottlebrush copolymer additives in a linear PLA matrix, blend films are characterized by water contact angle (WCA), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and optical microscopy measurements. Our analysis shows that bottlebrush copolymers with mixed PDMS and PLA side-chains spontaneously segregate to the top surface, as demonstrated by increased hydrophobicity, a significant excess of silicon at the top surface, and an absence of lateral phase separation in atomic force microscopy (AFM) and optical microscopy measurements. Bottlebrush copolymer additives are compared with diblock copolymer PLA-*b*-PDMS additives of a similar composition and with pure PDMS additives, and we find that bottlebrush copolymers segregate more strongly than diblock copolymers and produce more uniform films compared with PDMS homopolymer. This study shows that low concentrations of functional bottlebrush copolymer additives can introduce new surface properties in polymer films through a rapid and spontaneous demixing process.

Experimental Section

Materials

Monoaminopropyl terminated polydimethylsiloxane - asymmetric (M_n 2114 g mol⁻¹, 93% amino functionalized, as determined by ¹H NMR) (PDMS2k-NH₂) and monohydride terminated polydimethylsiloxane – asymmetric (M_n 6340 g mol⁻¹, 81% silane functionalized as determined by ¹H NMR) (PDMS6k-SiH) were purchased from Gelest Inc. *cis*-5-Norbornene-*exo*-2,3-dicarboxylic anhydride (NB-OH), triethyl amine, dichloro (1,5-cyclooctadiene) platinum (II), and D, L-lactide were purchased from Sigma Aldrich. Modified Grubb's second generation catalyst ((H₂IMes)(pyr)₂(Cl)₂RuCHPh)³⁷ and N-(hydroxypentanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide² were prepared as previously reported. D, L-lactide was recrystallized from ethyl acetate twice prior to use. All other reagents were used as received.

Synthesis of 2k PDMS macromonomer, PDMS2k-NB. PDMS2k-NH₂ (6.98 g, 3.30 mmol), triethyl amine (60 mg, 0.59 mmol), NB-OH (561.6 mg, 3.42 mmol) and 200 mL anhydrous toluene were added to a 250 mL round bottom flask equipped with a stir bar. The reaction flask was attached to a Dean-Stark trap with a condenser and allowed to react at 120 °C for 18 hours. The product was concentrated by rotary evaporation, and the final product isolated by silica gel chromatography with 9:1 hexanes : ethyl acetate as the eluent. Number average molecular weight and end-group functionality are determined by end-group analysis from ¹H NMR with respect to the terminal –CH₃. The molecular weight distribution, *D*, is calculated from GPC calibrated with polystyrene standards. PDMS2k-NB: M_n 2 260 g/mol (DP 27), 72 % norbornene functionalized, *D* 1.16, yield 1.4 g (26 % isolated yield). ¹H NMR spectra of the final product is provided in the Supporting Information Figure S1.

Synthesis of 6k PDMS macromonomer, PDMS6k-NB. PDMS6k-SiH (5.36 g, 0.845 mmol) and allyl amine (1 mL, 1 g, 17.5 mmol) were added to a 100 mL round bottom flask with 5 mL anhydrous toluene, followed by addition of catalyst solution (5 mg dichloro (1,5-cyclooctadiene) platinum (II) in 2mL dichloromethane (DCM)). The reaction proceeded in a 50 °C oil bath for 4 hours. The crude product was washed with 1M HCl to remove excess amine, and the organic phase was collected and dried with MgSO₄. The organic phase was concentrated *in vacuo* to yield PDMS6k-NH₂. PDMS6k-NH₂ was converted to PDMS6k-NB by the same procedure stated above for PDMS2k-NB and purified by column chromatography using a DCM/hexanes gradient eluent, starting at 1:3 DCM : hexanes and gradually increasing the DCM content to 1:1 DCM : hexanes. Number average molecular weight and end-group functionality are determined by end-group analysis from ¹H NMR with respect to the terminal –CH₃. The molecular weight distribution, *D*, is calculated from GPC calibrated with polystyrene standards. PDMS6k-NB: *M_n* 6 780 g/mol (DP 88), 40 % norbornene functionalized, *D* 1.17, yield 582 mg (10 % isolated yield). ¹H NMR spectra is provided in the Supporting Information Figure S2.

Synthesis of PDMS bottlebrushes, P(NB-PDMS-X)_n. All reactions were carried out in an oxygen and water-free glove box. The following is a representative synthesis of P(PDMS2k)₆₂. PDMS2k-NB (100 mg, 0.044 mmol) was added to a glass vial, equipped with a stir bar. Anhydrous, degassed DCM was added to the vial for a final solution concentration of 0.05 M (0.8 mL). A stock solution of Grubb's modified second generation catalyst was prepared in a separate vial (2.0 mg, 0.002 mmol, in 1.5 mL DCM). For a target backbone DP of 100, 0.0043 mmol of catalyst (100 μL) was added to the stirring macromonomer flask and allowed to react for 2 hours at room temperature. To quench the reaction, the vial was removed from the glove box and approximately 100 μL of butyl vinyl ether was added. The product is a viscous, semi-

clear liquid and was concentrated *in vacuo* prior to characterization by GPC and NMR. The properties of PDMS bottlebrushes are presented in Table 1.

Synthesis of linear PLA for matrix (PLA-18k). Linear PLA was synthesized *via* ring opening polymerization of D, L-lactide in the presence of stannous octoate and a norbornenyl-alcohol using a procedure modified from a previous report.³⁸ Lactide (15.3 mmol, 2.37 g), N-(hydroxypentanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (0.22 mmol, 58.5 mg) and stannous octoate (0.13 mmol, 53 mg) were added to a 50 mL round bottom flask, and the flask was purged and backfilled with nitrogen three times. The reaction proceeded for 5 hours at 120 °C. The polymer was collected by precipitation in methanol and dried *in vacuo* to yield PLA-18k (M_n 17500 g mol⁻¹ $\bar{D}$ 1.36, yield 1.62 g, 68 % isolated yield).

Synthesis of PLA macromonomer, PLA2k-NB. PLA2k-NB was synthesized following the above procedure. Lactide (17.18 mmol, 2.47 g), N-(hydroxypentanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (1.23 mmol, 0.31 g) and stannous octoate (0.04 mmol, 18 mg) reacted for 3 hours at 120 °C and collected by precipitation. PLA2k-NB M_n 2600 g/mol determined by ¹H NMR, $\bar{D}$ 1.48 determined by GPC with PS standards, yield 1.70 g, 67 % isolated yield.

*Synthesis of PLA/PDMS Bottlebrush Copolymers, P(XPDMS-*co*-YPLA).* All reactions were carried out in an oxygen and water-free glove box. The synthesis of P(23PDMS-*co*-77PLA)₆₁ is described as a representative procedure. PDMS2k-NB (22.1 mg, 0.00978 mmol) and PLA2k-NB (76.8 mg, 0.0295 mmol) were added to a clean glass vial, equipped with a stir bar. Anhydrous DCM was degassed by bubbling nitrogen. Stock catalyst solution was prepared in a second vial (1 mL, 2.84 mg Grubb's modified second generation catalyst in DCM). DCM was added to the flask containing macromonomer to create a total molar concentration of PDMS and PLA macromonomer of 0.05 M (0.78 mL). Once dissolved, 100 μ L of catalyst solution was

added to the reaction vial and allowed to stir at room temperature for 2 hours before quenching by addition of butyl vinyl ether. Bottlebrush polymers were precipitated in cold methanol and dried *in vacuo* prior to characterization. The absolute molecular weight of all bottlebrushes was measured by gel permeation chromatography (GPC) with multi-angle laser light scattering (MALLS) analysis along with dn/dc measurement from a refractive index (RI) detector. See Table 2 properties of bottlebrush copolymers P(XPDMS-*co*-YPLA)₁₀₀. ¹H NMR spectra is shown in Figure S3.

Film preparation. All films, except those used for XPS (described in XPS experimental), were cast on cleaned silica wafers. Wafers cleaned by sonication in 2 wt % soap solution in water, DI water, and isopropyl alcohol for 30 minutes per solvent. After drying, polymer solutions (20 mg mL⁻¹ in chloroform) were spin casted for 60 s at 1500 rpm and 30 s at 300 rpm, typically producing films ~100 nm. Thermal annealing of films was performed by heating films to 100 °C for 2 hours on a hot plate in a nitrogen glove box and allowed to cool to room temperature before analysis.

Gel-Permeation Chromatography (GPC). Polymer molecular weights and molecular weight dispersities were obtained using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10000 Å pore sizes), an Agilent variable wavelength UV/vis detector, a Wyatt technology HELEOS II multiangle laser light scattering (MALLS) detector ($\lambda = 658$ nm), and a Wyatt Technology Optilab reX RI detector. This system enables GPC with simultaneous refractive index (GPC-RI), UV/vis (GPC-UV/vis), and MALLS detection. THF was used as the mobile phase at a flow rate of 1 mL/min at 40 °C. For bottlebrush polymer synthesis, macromonomer conversion was determined by comparing the integrated areas corresponding to bottlebrush polymer and unreacted macromonomer. Bottlebrush polymer dn/dc values were

calculated assuming 100% mass recovery and correcting the injected mass to account for unreacted macromonomer.

Nuclear Magnetic Resonance Spectroscopy (NMR). Proton-NMR (^1H NMR) spectra were recorded using tetramethylsilane as internal standard in CDCl_3 on a 400 MHz Bruker multinuclear spectrometer. Samples were placed in 5 mm o.d. tubes with the concentration of 10 mg/mL.

Differential Scanning Calorimetry (DSC). DSC experiments were conducted employing two different protocols using a TA Instruments Q2000 calorimeter, calibrated for the liquid nitrogen cooling system (LNCS) using an indium standard and a helium flow rate of 25 mL/min. For samples involving PDMS, blends were placed in the calorimeter (using a Tzero aluminum pan) held at standby at 40 °C. The sample was cooled to -150 °C at a rate of 10 °C/min, held isothermally at -150 °C for 5 minutes, and subsequently heated to 0 °C at a rate of 10 °C/min and held at isothermally 0 °C for 5 minutes before starting another heating and cooling cycle. Bottlebrush copolymer samples were placed in the calorimeter (using a Tzero aluminum pan) held at standby at 40 °C. The sample was cooled to -150 °C at a rate of 10 °C/min, held isothermally at -150 °C for 5 minutes, and subsequently heated to 100 °C at a rate of 10 °C/min and held at isothermally 100 °C for 5 minutes before starting the cycle again. At least two cool/heat cycles were performed for each sample.

Contact Angle goniometry. Static contact angle measurements of DI water on polymer films were carried out using a Drop Shape Analyzer DSA 100 (Krüss Instruments) at ambient conditions. Water contact angles were measured immediately after contact with water. Measurements were repeated at least on three different spots per substrate per sample. The final reported values given represent an average and standard deviation of each film.

X-ray Photoelectron Spectroscopy (XPS, PHI Quantera SXM). XPS measurements were conducted using a PHI Quantera XPS, which uses a focused monochromatic Al K α X-ray (1486.7 eV) source for excitation and a 50 W, 15 kV and 200 μ m diameter X-ray beam for sample analysis. The XPS survey scan spectra were recorded in 0.5 eV steps with a pass energy of 140 eV. High resolution scan spectra of C1s were recorded in 0.1 eV steps with a pass energy of 26.0 eV. Low energy electrons and Ar⁺ ions were conducted for specimen neutralization in each measurement. The take-off angle is 45 degrees (penetration depth of 3 – 5 nm). Thin-film samples for XPS were prepared by dissolving polymer or polymer blends in chloroform at 20 mg/mL, filtering solutions and spin-casting onto cleaned ITO substrates at 1500 rpm for 60 s followed by 300 rpm for 30 s.

Atomic Force Microscopy (AFM). AFM analysis was performed using a Dimension 3000 (Digital Instruments) system. Height and phase images were recorded in tapping mode using silicon probes that have a spring constant of approximately 40 N/m and an aluminum reflex coating. The parameters used for data acquisition were approximately 1.0 Hz scan frequency, 5 μ m x 5 μ m scan area, and 512 x 512 image resolution. 2nd order flattening was used for compensation of sample tilt and enhancement of image contrast.

Optical Microscopy (OM). Microscopy images were taken using a Zeiss Axioplan optical microscope in reflectance mode. Bright field and dark field images presented in the Supporting Information were taken using a Nikon Eclipse LV-100.

Results

PDMS Bottlebrush Polymer Synthesis and Characterization

PDMS bottlebrush polymers were synthesized using “grafting-through” ring-opening metathesis polymerization (ROMP) of norbornene-terminated PDMS macromonomers, as shown in Scheme 1. Norbornene-terminated PDMS macromonomers PDMS2k-NB and PDMS6k-NB were prepared by end-group modification of commercially available linear PDMS. For PDMS2k-NB, the amino terminus of PDMS2k-NH₂ was directly converted to a ROMP-active norbornene group by condensation with NB-OH in the presence of triethyl amine (see Scheme 1). PDMS6k-NB an additional step was necessary to convert a silane terminus to an amine, which was followed by condensation with NB-OH yielding PDMS6k-NB. Resulting end-group functionality, degree of polymerization, and number average molecular weights, M_n , of PDMS macromonomers was determined by ¹H NMR end-group analysis. Macromonomer polydispersity index (dispersity $\bar{D}$) was calculated by GPC. PDMS2k-NB has M_n 2260 g mol⁻¹ ($\bar{D}$ 1.16) and PDMS6k-NB has M_n 6780 g mol⁻¹ ($\bar{D}$ 1.17). A detailed ¹H NMR analysis for intermediates and macromonomer products are presented in the Supporting Information.

Scheme 1. Synthesis of PDMS bottlebrush polymers $\text{P(PDMS-}X\text{)}_n$, where X denotes the molecular weight, M_n , of each side-chain in g/mol and n denotes the degree of polymerization (DP) of backbone.

Table 1: Chemical and thermal properties of PDMS bottlebrush polymers P(PDMS2k)_n and P(PDMS6k)_n, where *n* denotes the degree of polymerization (DP) of backbone.

Polymer	M_w^a	$\bar{D}^b$	[MM]/		% Conv. ^c	T_g
	[g/mol]	$[M_w/M_n]$	[cat.] ^c	DP _{BB} ^d		
P(PDMS2k) ₃₉	89 000	1.14	50	39	88	-123
P(PDMS2k) ₆₂	141 000	1.14	100	62	90	-123
P(PDMS2k) ₁₀₉	247 100	1.32	200	109	81	-124
P(PDMS2k) ₁₂₇	286 600	1.30	300	127	87	-123
P(PDMS6k) ₂₂	147 900	1.18	50	22	87	-122
P(PDMS6k) ₄₄	296 500	1.21	100	44	84	-122
P(PDMS6k) ₉₇	654 300	1.39	150	97	84	-122
P(PDMS6k) ₁₀₅	709 200	1.49	300	105	88	-123

^a Absolute weight averaged molecular weight, M_w , of bottlebrush polymers calculated from GPC light-scattering analysis. ^b Polymer dispersity index from GPC relative to monodisperse PS standards. ^c Ratio of macromonomer to catalyst in ROMP synthesis. ^d Calculated using M_w from light-scattering for bottlebrush polymers and $M_{branch} = 2260$ g/mol for PDMS2k and $M_{branch} = 6780$ g/mol for PDMS6k. ^e Conversion of NB-PDMS during ROMP calculated using relative mass values from GPC-RI analysis.

Figure 2: Gel permeation chromatography (GPC) traces of PDMS X -NB macromonomers (dashed lines) and P(PDMS- X) $_n$ bottlebrush polymers (solid lines) with 2 kg/mol (top) and 6 kg/mol (bottom) PDMS side-chains.

ROMP of the PDMS macromonomers produced PDMS bottlebrushes with 2260 and 6780 g/mol side-chains and backbone DPs from 22 to 127. Detailed properties of all PDMS bottlebrush polymers are presented in Table 1. PDMS bottlebrush polymers with 2.3 kg/mol side-chains were synthesized with backbone DPs up to 127, resulting in molecular weights as high as 286,600 g/mol. PDMS bottlebrush polymers with 6.8 kg/mol side-chains were

synthesized with backbone DPs up to 105 with molecular weights reaching 709,200 g/mol. The molecular weight dispersity $\bar{D}$ was below 1.5 for all samples.

Thermal properties of PDMS bottlebrushes were studied by differential scanning calorimetry (DSC). All bottlebrush PDMS bottlebrush polymers exhibited a glass transition temperature, T_g , a crystal melting temperature, T_m , and a crystallization temperature, T_c (see the Supporting Information Figure S4 and Table S2). These transition temperatures were found to be independent of bottlebrush DP and only weakly dependent on side-chain molecular weight, as shown in Table 1 and Supporting Information Table S2.

As shown in Figure 2 and Table 1, the conversion of PDMS macromonomer estimated from GPC analysis is higher than 80 % for all samples. ^1H NMR analysis also indicates full conversion of the norbornene-functionalized macromonomer PDMS-NB. However, PDMS-NH₂ has a significantly lower dn/dc compared with PDMS-NB and is not detected by GPC. Careful ^1H NMR analysis of the PDMS macromonomers and final bottlebrush polymers is presented in the Supporting Information and indicates that PDMS-NH₂ impurities are present in the linear PDMS macromonomers. These impurities cannot be removed by precipitation since both PDMS macromonomer and bottlebrushes are liquids and have similar T_g values. Thus, while we cannot prepare pure PDMS bottlebrush polymers, we are able to achieve high-purity bottlebrush copolymers containing PLA and PDMS side-chains since, as described below, the copolymers are powdery and can be purified by re-precipitation in methanol.

Synthesis of PDMS/PLA bottlebrush copolymers

Bottlebrush copolymers with mixed PDMS and PLA side-chains were synthesized in a one-pot grafting-through ROMP of both PLA2k-NB (M_n 2600 g/mol) and PDMS2k-NB (M_n 2260 g/mol) macromonomers (Scheme 2). The resulting bottlebrush copolymers have PDMS and PLA side-chains and are denoted as P(*X*PDMS-*co*-*Y*PLA)_{*n*}, where *X* and *Y* represent the target molar fraction of PDMS and PLA side-chains, respectively and *n* represents the final bottlebrush backbone degree of polymerization. To investigate the polymer properties as a function of side-chain composition, we systematically varied the amount of PDMS side-chains in each bottlebrush copolymer while keeping the target backbone DP constant (target *n* = 100). All bottlebrush copolymers were solid at room temperature, even with only 25 mol% PLA side-chains, allowing for purification by precipitation in methanol to remove any unreacted PDMS macromonomer. The final ratio of PDMS to PLA side-chains in resulting copolymers, P(74PDMS-*co*-26PLA)₅₆, P(46PDMS-*co*-54PLA)₆₅, and P(23PDMS-*co*-77PLA)₆₁ was determined by ¹H NMR to be 74, 46, and 23 mol% PDMS2k-NB, respectively (see Table 2 and Supporting Information Figure S3). The PDMS composition of the bottlebrush copolymers was slightly lower than the target composition, due to the presence of unfunctionalized PDMS macromonomer, which is removed by precipitation in methanol. Bottlebrush copolymer polymer purity was confirmed by GPC to be greater than 98% in all cases.

Scheme 2. Synthesis of bottlebrush copolymers $P(XPDMS-co-YPLA)_n$ with mixed PDMS and PLA sidechains is carried out in a one-pot ROMP. The resulting polymers have 74, 46, or 23 mol % PDMS sidechains.

Table 2: Properties bottlebrush copolymers with PDMS and PLA side-chains

Sample ^a	M_w [g/mol] ^b	$\bar{D}$ ^c	f_{PDMS} ^d	dn/dc	% Conv. ^e	$T_{g,PDMS}$ (°C)	$T_{g,PLA}$ (°C)
P(74PDMS- <i>co</i> -26PLA) ₅₆	132 000	1.24	74.0	0.025	99	-122.2	37.9
P(46PDMS- <i>co</i> -54PLA) ₆₅	162 000	1.32	46.2	0.040	98	-121.8	45.7
P(23PDMS- <i>co</i> -77PLA) ₆₁	153 500	1.28	22.8	0.048	100	----	47.3

^a Backbone degree of polymerization calculated by dividing bottlebrush M_w by a weighted average of side-chain molecular weight $M_{branch} = X_{PDMS}(2260) + X_{PLA}(2600)$. ^b Absolute M_w calculated from GPC light-scattering analysis with reported dn/dc values. ^c From GPC relative to monodisperse PS standards. ^d Percentage of PDMS side-chains in final bottlebrush copolymer, as determined by ¹H NMR. ^e Mass fraction of bottlebrush polymer in the final isolated product, determined by GPC relative to PS standards. The remaining fraction is attributed to free macromonomer.

Thermal properties of bottlebrush copolymers were analyzed by differential scanning calorimetry. We anticipate two distinct T_g s associated with PDMS (-122 °C) and PLA (50 °C). Results are summarized in Table 2 and Supporting Information Figure S4. When PLA content is 25%, the T_g for PDMS is -122 °C while T_g for PLA is only 38 °C. The suppression of PLA T_g suggests that the low fraction of PLA side-chains cannot phase separate into a pure phase³⁹. As PLA content is increased to 50%, the T_g for PDMS is unchanged while T_g for PLA increases to 45 °C. This suggests that both side-chains can phase separate along the backbone into nearly pure domains. Finally, when PLA content is increase to 75%, the T_g for PDMS is entirely suppressed, while T_g for PLA is approximately 47 °C. This suggests that PDMS is not phase-separating when the concentration of side-chains is too low. No PDMS crystallization is

observed in any bottlebrush copolymer sample, as was observed for PDMS bottlebrush polymers.

Figure 3. GPC traces for PDMS/PLA bottlebrush copolymers and starting macromonomers showing minimal traces of macromonomer in final copolymer product

The surface properties of pure bottlebrush copolymer films with thickness of approximately 100 nm were characterized by contact angle measurements. The water contact angles (WCA) of $P(23PDMS-co-77PLA)_{61}$, $P(46PDMS-co-54PLA)_{65}$ and $P(74PDMS-co-26PLA)_{56}$ bulk films were $95 \pm 0.7^\circ$, $108 \pm 0.3^\circ$, and $107 \pm 1^\circ$, respectively, while the WCA of pure linear PLA films is $66 \pm 0.9^\circ$. The WCA of $P(74PDMS-co-26PLA)_{56}$ and $P(46PDMS-co-54PLA)_{65}$ films is the same as pure PDMS elastomer (Table 3), suggesting that side-chains can partially rotate along the main backbone to form a pure PDMS wetting layer at the free surface. While all films were

hydrophobic, the extent of hydrophobicity increased with PDMS composition. Optical microscopy of P(74PDMS-*co*-26PLA)₅₆ films were uneven and rough, whereas P(46PDMS-*co*-54PLA)₆₅ and P(23PDMS-*co*-77PLA)₆₁ films appear to be smooth (Supporting Information Figure S5). The roughness in bottlebrushes with high PDMS content is expected, as these materials are more liquid-like and polymer films undergo de-wetting when annealed near or above the glass-transition temperature.⁴⁰

Bottlebrush copolymer additives and thin-film properties

In prior work with nearly athermal blends of bottlebrush and linear polymers,¹¹ we demonstrated that miscibility is controlled by relative lengths of matrix and bottlebrush side-chains (N_m/N_{sc}). When $N_m/N_{sc} < 2$, the matrix polymer could "wet" the bottlebrushes and enable their dispersion. When $N_m/N_{sc} > 8$, the bottlebrushes were less wettable, so the constituents underwent a slow demixing process that drove the bottlebrushes to the interfaces; this allowed linear chains to gain conformational entropy in the interior of the film. In the present study, we consider the behavior in non-athermal systems of PDMS/PLA bottlebrush copolymers reported above in blends with linear PLA (M_n 17.5 kg/mol), where $N_m/N_{sc} \sim 8$, $f_{PDMS} = 23, 46$, or 74 mol % PDMS side-chains, and the bottlebrush loading is either 1 or 5 wt %. PDMS and PLA are highly incompatible (Flory-Huggins segment-segment interaction parameter $\chi \approx 1.4$ at 298 K for a reference volume of $118 \text{ \AA}^3$)⁴¹⁻⁴² so PLA bottlebrush arms will act as compatibilizers to stabilize the bottlebrush additives in the film. The surface energies of PDMS and PLA are 19.8 mN/m and 42 mN/m, respectively,⁴³⁻⁴⁵ therefore, we expect PDMS-based bottlebrushes to de-mix and accumulate at the air interface. We anticipate that bottlebrushes may also accumulate at the

bottom interface,⁴⁶⁻⁴⁷ but the objective of these studies is to tailor surface properties, so we do not emphasize characterization of the buried interface in this work.

To determine if bottlebrush copolymers spontaneously segregate to the top of thin film blends, we first measured the water contact angle (WCA) for bulk PLA films and found a value of $65.7 \pm 1^\circ$. As a reference, bulk PDMS is extremely hydrophobic with a measured water contact angle of $107 \pm 1.3^\circ$. We then measured the WCA for all blends and observed significant increases (by more than 20°) with only 1 wt % bottlebrush. Blends with 5 wt % bottlebrush additives showed further increases in contact angle, by up to 30° . Therefore, bottlebrush copolymer additives accumulate at the free surface and introduce hydrophobic behavior, where the extent of hydrophobicity is enhanced with loading. Contact angles as a function of bottlebrush copolymer loading and side-chain composition are reported in Table 3 and Figure 4. All films are hydrophobic ($\text{WCA} > 90^\circ$), with the exception of 1 wt % P(23PDMS-*co*-77PLA)₆₁ which has a WCA of 85° owing to the high PLA content and the low loading of the material. The WCA for 5 wt % blends increased by an average of 6.1° compared with the 1 wt % blends for all compositions of additives. Similar to results from pure bottlebrush copolymer contact angles, a higher content of PDMS side-chains in the copolymer additives results in higher contact angle values for the blends. In all cases, the water contact angle for blends was less than the value for the corresponding pure bottlebrush copolymer, indicating the presence of some PLA at the top film interface.

Figure 4. Water contact angle (WCA) of bulk PLA films (white bar) and films blended with 1 wt % (gray bar) or 5 wt % (black bar) bottlebrush copolymers in bulk PLA with respect to WCA of bulk PLA films. Copolymer additives, P(XPDMS-*co*-YPLA), are labeled by the ratio of PDMS (X) to PLA (Y) side-chains and represent blends from P(74PDMS-*co*-26PLA)₅₆, P(46PDMS-*co*-54PLA)₆₅, and P(23PDMS-*co*-77PLA)₆₁.

Film uniformity and stability were evaluated by optical microscopy of blend films immediately after spin-casting and after thermal annealing. Bulk PLA films are smooth and featureless before and after annealing, while obvious phase separation is observed in PLA films containing either 1 or 5 wt % linear PDMS additive (M_n 2110 g/mol) (Figure 5 and Supporting Information Figures S6 and S7), which is expected due to the strong incompatibility between PLA and PDMS. Blend films with bottlebrush copolymer additives are uniform both before and after thermal annealing, with the exception of films with a 5% loading of P(74PDMS-*co*-26PLA)₅₆ which phase separates after thermal annealing. This suggests that PLA side-chains are effective

compatibilizers to prevent lateral phase separation, provided the PLA content is high enough. The nanoscale morphology of the film surface was further analyzed by both AFM and dark-field microscopy measurements and is discussed below.

Figure 5. Optical micrographs of films cast with 5 wt% bottlebrush copolymer additives (A – F) and linear PDMS (G-H) before and after thermal annealing (right column). A,B) P(23PDMS-*co*-

77PLA)₆₁; C,D) P(46PDMS-*co*-54PLA)₆₅; E,F) P(74PDMS-*co*-26PLA)₅₆; G,H) linear PDMS2k. Scale bar 50 μ m.

The contact angle and microscopy results indicate that bottlebrush copolymer additives segregate to the top film surface without large-scale phase segregation, with the exception of 5 wt % P(74PDMS-*co*-26PLA)₅₆. For comparison, a series of PDMS-*b*-PLA diblock copolymers with roughly 25, 50, and 75 wt % PDMS were synthesized and used as additives in PLA films (see Supporting Information Table S1). Blend films with 1 and 5 wt % diblock copolymer additives appeared uniform before and after thermal annealing (See Supporting Information Figures S6 and S7). As expected, PDMS-*b*-PLA additives increase the film WCA due to segregation to the film surface, but the increase in WCA is smaller compared with bottlebrush copolymer additives. Linear diblock additives increased the WCA up to 87.3° and 96.5° for 1 and 5 wt % loading compared with 93.4° and 99.5° for bottlebrush copolymer additives (Table 3 and Supporting Information Table S3). The difference is greater than the uncertainty in the WCA values, which is less than 1° for all samples. The stronger effect of bottlebrushes may be due to a combination of enthalpic and entropic effects that drive bottlebrushes to interfaces. Diblock copolymers may also be forming micelles rather than segregating to the film interface. The contact angle values of blend films containing linear diblock copolymer decreased with higher PDMS compositions in the diblock, which is consistent with the formation of diblock copolymer micelles in the film interior^{17, 48}

Blend films containing bottlebrush copolymers were analyzed by XPS to determine the composition at the top surface. The data from XPS analysis corresponds to the elemental composition within the top 3 – 5 nm of each film, and PDMS homopolymer, PLA homopolymer,

and pure bottlebrush copolymers were measured as references. XPS data were analyzed by comparing relative peak areas between carbon, oxygen and silicon (C_m , O_m , and Si_m) and adjusting for sensitivity factors (Table 3). We also calculated the expected peak ratios for carbon, oxygen and silicon (C_c , O_c and Si_c) based on the known chemical structures for PDMS and PLA polymers and assuming uniform mixing of PDMS and PLA in the films (see SI for a detailed explanation). For the single component films, the measured and calculated C:O ratios were generally in good agreement, within 3 % for all samples. Qualitatively, the measured Si contents trend as expected: P(74PDMS-*co*-26PLA)₅₆ has the highest Si content, and P(23PDMS-*co*-77PLA)₆₁ has the lowest. We measured higher Si contents in P(23PDMS-*co*-77PLA)₆₁ relative to the calculated values, while the Si content was lower than the calculated value for P(74PDMS-*co*-26PLA)₅₆ and P(46PDMS-*co*-54PLA)₆₅. This suggests that the PDMS side-chains may segregate towards the top film surface when the PDMS content is low, while the side-chains are more uniformly mixed for bottlebrushes with higher PDMS content.

Table 3: Compositional values of C, O, and Si for calculated values and measured results, determined by XPS measurements in pure component and blend thin films.

Sample	Calculated Ratios			Measured Ratios			BBP	WCA (°)
	C _c	O _c	Si _c	C _m	O _m	Si _m	wt %	
Linear PLA	60.0	40.0	0	63.7	36.3	0	N/A	65.7 ± 0.9
Linear PDMS	50.0	25.0	25.0	49.5 ^a	27.9 ^a	22.6 ^a	N/A	107 ± 1.3 ^b
P(74PDMS- <i>co</i> -26PLA) ₅₆	52.5	28.8	18.8	51.8	30.3	17.9	N/A	107 ± 1.0
P(46PDMS- <i>co</i> -54PLA) ₆₅	54.7	32.1	13.3	53.2	34.1	12.7	N/A	108 ± 0.3
P(23PDMS- <i>co</i> -77PLA) ₆₁	57.2	35.8	7.0	56.8	34.9	8.3	N/A	95 ± 0.7
1% P(74PDMS- <i>co</i> -26PLA) ₅₆	59.9	39.9	0.2	58.1	35.9	6.1	19.6	92.0 ± 0.5
5% P(74PDMS- <i>co</i> -26PLA) ₅₆	59.7	39.5	0.9	55.9	34.4	9.7	30.6	98.2 ± 0.2
1% P(46PDMS- <i>co</i> -54PLA) ₆₅	60.0	39.9	0.1	58.6	35.9	3.0	14.9	93.4 ± 0.6
5% P(46PDMS- <i>co</i> -54PLA) ₆₅	59.8	39.7	0.6	58.6	35.9	5.8	28.4	99.5 ± 0.5
1% P(23PDMS- <i>co</i> -77PLA) ₆₁	60.0	40.0	0.1	62.6	35.6	1.8	17.1	84.7 ± 0.2
5% P(23PDMS- <i>co</i> -77PLA) ₆₁	59.9	39.8	0.3	60.4	36.5	3.1	29.2	90.7 ± 0.4

^a XPS data from PDMS films reported by Sabata et. al.⁴⁹ ^b Estimated from measurements of PDMS elastomer prepared from Sylgard 184.

In the case of bottlebrush blends, the predicted elemental ratios were calculated from a mass balance by assuming the bottlebrushes were uniformly distributed throughout the thickness of the film (i.e. the calculated surface composition is the same as the bulk composition). If bottlebrush copolymers segregated to the free surface, then we should observe a higher measured Si content relative to calculated values. As shown in Table 3 and Figure 6, XPS results for blends reveal a

large increase in the Si content over the expected values. This demonstrates an excess of bottlebrush at the surface of the films, which is consistent with water contact angle measurements. The 1 wt % blends show 2 – 5 mol % Si content, whereas the expected content is less than 0.2 mol % for a homogeneous distribution of bottlebrush. The 5 wt % blends show a larger increase in the Si content, with Si compositions of 9.7, 5.8, and 3.1 mol % for P(74PDMS-*co*-26PLA)₅₆, P(46PDMS-*co*-54PLA)₆₅, and P(23PDMS-*co*-77PLA)₆₁, respectively. Blends with 5 wt % bottlebrush copolymer have a higher Si content than the 1 wt % blends, as expected.

Figure 6: XPS survey data for bottlebrush copolymer sample P(74PDMS-*co*-26PLA)₅₆ for films cast from 1 wt% blend (blue), 5 wt% blend (red) and 100 % bulk copolymer (black). Inset shows silicon signal increases with bottlebrush copolymer loading. Elemental compositions are calculated from oxygen (O 1s), carbon (C 1s) and silicon (Si 2p) signals present in all cases.

The measured silicon content is used to determine the mass fraction of each blend at the top surface. Based on measured XPS C_m:O_m:Si_m ratios for blends and homopolymer bottlebrush films, we determined the mass fraction of bottlebrush copolymers in the film surface is between

15 and 20 wt % for 1 wt % blends, and between 28 and 31 wt % for the 5 wt % blends. These results combined with contact angle and optical microscopy measurements prove that bottlebrush copolymers spontaneously segregate to the polymer-air interface during spin casting without macroscopic phase separation. The bottlebrush content of the top surface appears to be roughly independent of the PDMS content in the bottlebrush copolymers, which demonstrates that bottlebrush segregation is always favored in this materials system.

To further investigate the morphology of bottlebrush copolymer blend films, we characterized all films by AFM and dark field optical microscopy, and included pure PLA films as a reference. The surfaces of most films are relatively smooth, although we detect small apparent depressions in AFM height and phase images (see Figure 7 for pure PLA and PLA with P(46PDMS-*co*-54PLA)₆₅ additives, and Supporting Information Figures S8 and S9 for all films). These depressions are present in the PLA control sample, and the addition of bottlebrush additive has little impact in most cases. The exception is films with 5 wt% P(74PDMS-*co*-26PLA)₅₆ additive, which show dense, large holes. Perhaps this indicates the early stages of phase separation, or potentially the bottlebrush surface coating is dewetting.

One might imagine these depressions are PDMS domains, and the AFM tip is "sinking" when contacting these rubbery regions.⁴² However, we assign these features as holes based on the following arguments: First, AFM analysis reveals similar features in pure PLA films (Figure S10). Other studies have found similar holes in PLA fibers and films attributed to evaporative cooling and condensation of water droplets on the surface.⁵⁰⁻⁵¹ Second, dark field optical microscopy clearly demonstrates that these features are associated with significant topography: The edges of these features are strongly scattering, which is expected for deep holes. These data are reported in Supporting Information Figure S11.

Figure 7: AFM height and phase images of pure PLA (A,B) and P(46PDMS-*co*-54PLA)₆₅ bottlebrush copolymer blend unannealed films with 1 and 5wt % bottlebrush. A,B) Pure PLA films, C,D) 1 wt% P(46PDMS-*co*-54PLA)₆₅; E,F) P(46PDMS-*co*-54PLA)₆₅. Scale bar is 150 nm in all images.

Conclusions

We demonstrate the synthesis of PDMS bottlebrush polymers and PDMS/PLA bottlebrush copolymers by ROMP. This synthesis method enables the preparation of well-defined, highly branched PDMS bottlebrush copolymers with tunable thermal properties. The thermal properties were dictated by the molar ratios of PDMS and PLA side-chains, and control over thermal

properties may be of interest for lubricants, adhesives, and coatings. These materials exhibit surfactant-like properties in thin film blends with linear PLA: contact angle goniometry, XPS, and microscopy demonstrate a spontaneous accumulation of these additives at the film surface without lateral phase segregation. Bottlebrush polymers were found to enrich the film surface more strongly than linear block copolymers of PDMS-*b*-PLA, and the surface contact angle was tunable by varying the composition and quantity of added bottlebrush copolymer. This work demonstrates that low-surface energy bottlebrush copolymer additives can be used to introduce new surface properties in polymer films, such as creating a hydrophobic surface in a hydrophilic polymer film, which has potential applications in fouling reduction. Future work will explore the use of tailored bottlebrush copolymers to introduce different surface functionalities through entropically- and enthalpically-mediated segregation.

ASSOCIATED CONTENT

Supporting Information.

Synthesis of linear PDMS-*b*-PLA diblock polymers, ¹H NMR spectra of PDMS macromonomers, DSC thermographs, contact angle results of linear diblock blends, POM images of thin films, and additional AFM images of films after annealing are shown in Supporting Information. A detailed explanation of XPS calculations is also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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