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Effects of Grafting Density on Block Polymer Self-Assembly: From Linear to Bottlebrush

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ABSTRACT: Grafting density is an important structural parameter that exerts significant influences over the physical properties of architecturally complex polymers. In this report, the physical consequences of varying the grafting density (z) were studied in the context of block polymer self-assembly. Well-defined block polymers spanning the linear, comb, and bottlebrush regimes ($0 \leq z \leq 1$) were prepared *via* grafting-through ring-opening-metathesis polymerization (ROMP). ω -norbornenyl poly(D,L-lactide) (**PLA**) and polystyrene (**PS**) macromonomers were copolymerized with discrete co-monomers in different feed ratios, enabling precise control over both the grafting density and molecular weight. Small-angle X-ray scattering (SAXS) experiments

demonstrate that these graft block polymers self-assemble into long-range-ordered lamellar structures. For seventeen series of block polymers with variable z , the scaling of the lamellar period with the total backbone degree of polymerization ($d^* \sim N_{bb}^\alpha$) was studied. The scaling exponent α monotonically decreases with decreasing z and exhibits an apparent transition at $z \approx 0.2$, suggesting significant changes in the chain conformations. Comparison of two block polymer systems, one that is strongly segregated for all z (**System I**) and one that experiences weak segregation at low z (**System II**), indicates that the observed trends are primarily caused by the polymer architectures, not segregation effects. A model is proposed in which the characteristic ratio (C_∞), a proxy for the backbone stiffness, scales with N_{bb} as a function of the grafting density: $C_\infty \sim N_{bb}^{f(z)}$. The scaling behavior disclosed herein provides valuable insights into conformational changes with grafting density, thus introducing opportunities for block polymer and material design.

TOC:

Block polymer self-assembly is a powerful process that connects molecular and materials design.¹⁻⁶ Due to their covalently linked yet chemically distinct blocks, block polymers provide

access to a wide range of periodic structures by balancing competing entropic and enthalpic demands. Linear AB diblock polymers feature the simplest possible block connectivity and architecture, yet they still afford rich opportunities to tune structure and properties through the block volume fraction (f), binary block-block interaction parameter (χ), and total degree of polymerization (N). Due to this versatility, the self-assembly of block polymers has been exploited in many practical applications spanning all areas of science and technology.

Recent advances in polymer chemistry have enabled the precise synthesis of polymers with non-linear architectures.^{7,8} Introducing architectural complexity expands the opportunities for block polymer design. We recently reported the efficient synthesis of graft polymers with controlled grafting density (z), defined as the average number of polymer side chains per backbone repeat unit.⁹ In the present report, we study the effects of grafting density on the scaling of the lamellar period (d^*) with the total backbone degree of polymerization (N_{bb}). The scaling of d^* reflects steric demands and penalties to chain stretching, thus providing valuable insight into the physical consequences of varying polymer architectures. In addition, d^* is an attractive parameter to study because it has an unambiguous physical definition (unlike potentially model-dependent parameters such as χ) and can be directly measured by scattering and electron microscopy.¹⁰

Chart 1. Self-assembly of linear and bottlebrush diblock polymers into lamellae.

Chart 1 illustrates the self-assembly of linear ($z = 0$) diblock polymers into lamellar morphologies. For symmetric linear diblock polymers, arguments based on free energy demands accurately predict the scaling behavior ($d^* \sim N_{bb}^\alpha$). The scaling exponent α is 1/2 in the weak segregation limit ($\chi N_{bb} \approx 10.5$) and plateaus at 2/3 in the strong segregation limit ($\chi N_{bb} \gg 10.5$).^{11,12} The small scaling exponent is intrinsically related to the coil-like chain conformations. In contrast, reports of scaling behavior for block polymers with bottlebrush ($z = 1$) and other complex, non-linear architectures are limited due to the synthetic challenges associated with (1) precisely controlling the architecture, molecular weight, and composition and (2) efficiently preparing multiple samples to study trends.

Bottlebrush polymers have recently emerged as an advanced class of non-linear architectures that manifest unique physical, mechanical, and dynamic properties.¹³⁻²⁰ Like their linear analogues, bottlebrush diblock polymers can also access lamellar morphologies (Chart 1).

However, bottlebrush block polymers display much larger scaling exponents ($\alpha = 0.8\text{--}0.9$),²¹⁻²⁴ consistent with extended backbone conformations. Steric repulsion between the densely grafted side chains imparts a certain bending rigidity to the backbone, which can be modeled as a wormlike chain.²⁵⁻²⁸ The unique properties of bottlebrush polymers have been previously exploited for applications in photonics,²⁹⁻³² lithography,^{33,34} surface coatings.³⁵ For example, the bottlebrush architecture minimizes chain entanglement and promotes rapid self-assembly to structures with ultra-large d^* , enabling the fabrication of photonic materials that reflect visible and even infrared radiation. In contrast, such materials are generally inaccessible using linear and low- z analogues due to the ultra-high molecular weights required as well as their low entanglement molecular weights.

The effects of grafting density on the rheological properties of homopolymers have received tremendous interest.³⁶⁻⁴⁴ However, the impacts of grafting density on block polymer self-assembly have not been explored.⁴⁵⁻⁴⁸ Elucidating these physical principles is not only of fundamental importance but should also guide material design. With this mindset, we launched the study on block polymers with systematically modified grafting densities ($0 \leq z \leq 1$) spanning the linear, comb, and bottlebrush regimes. The self-assembly of these block polymers was examined by small-angle X-ray scattering (SAXS), allowing determination of the scaling behavior. These studies reveal vital information on the backbone conformations, and the determined scaling laws allow prediction of lamellar periods of direct relevance to the development of nanomaterials.

RESULTS AND DISCUSSION

Synthesis of block polymers with variable grafting densities (System I: Different diluents for each block). Ring-opening metathesis polymerization (ROMP) is a powerful strategy to

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3 synthesize well-defined bottlebrush polymers in a controlled and living manner.⁴⁹⁻⁵² We targeted
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5 poly(*D,L*-lactide)-*b*-polystyrene (**PLA-*b*-PS**) graft diblock polymers to permit comparisons with
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7 brush PLA-*b*-PS systems previously investigated in the context of self-assembly.²¹⁻²⁵ All
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9 polymerizations were carried out in CH₂Cl₂ at room temperature under an inert atmosphere. To
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11 vary the grafting density (Figure 1), the first block was synthesized by copolymerizing a **PLA**
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13 macromonomer ($M_n = 3230$ g/mol) with a discrete co-monomer (*i.e.*, diluent), **DME** (*endo,exo*-
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15 norbornenyl dimethyl ester, $M_n = 210$ g/mol). The grafting density (z) is precisely determined by
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17 the feed ratio according to Eq. 1:
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$$z = \frac{[\text{PLA}]_0}{[\text{PLA}]_0 + [\text{DME}]_0} \quad (1)$$

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Figure 1. Synthesis of $(\text{PLA}^z\text{-}r\text{-DME}^{1-z})_n\text{-}b\text{-}(\text{PS}^z\text{-}r\text{-DBE}^{1-z})_n$ block polymers (**System I**) featuring variable backbone degrees of polymerization ($N_{\text{bb}} = 2n = 44\text{--}363$) and grafting densities ($z = 1.00, 0.75, 0.50, 0.35, 0.25, 0.20, 0.15, 0.05, 0$).

After both co-monomers have been fully consumed (as verified by ^1H NMR), a mixture of a **PS** macromonomer ($M_n = 3990$ g/mol) and another discrete diluent, **DBE** (*endo,exo*-norbornenyl di-*n*-butyl ester, $M_n = 294$ g/mol), was introduced as the second block. The **PS/DBE** feed ratio was the same as the **PLA/DME** feed ratio in the first block. The determined reactivity ratios (block A:

$r_{\text{PLA}} = 0.92$, $r_{\text{DME}} = 1.11$; block B: $r_{\text{PS}} = 0.80$, $r_{\text{DBE}} = 1.16$) suggest that the copolymerization is statistically random with minimal compositional drift.⁹ Monitoring the instantaneous monomer concentrations over time indicates that the macromonomer and diluent are incorporated at approximately equal rates in each block, consistent with uniform z throughout the entire block polymer. The backbone degrees of polymerization (n) for the first and second blocks were equal and determined by the ratio of the total monomer concentration to catalyst (**G3**) concentration (Eqs. 2–3):

$$n = \frac{[\text{PLA}]_0 + [\text{DME}]_0}{[\text{G3}]_0} = \frac{N_{\text{bb}}}{2} \quad (2)$$

$$n = \frac{[\text{PS}]_0 + [\text{DBE}]_0}{[\text{G3}]_0} = \frac{N_{\text{bb}}}{2} \quad (3)$$

For **System I**, nine different series with variable grafting densities ($z = 1.00, 0.75, 0.50, 0.35, 0.25, 0.20, 0.15, 0.05$, and 0) were prepared. Each series includes five to seven block polymers with fixed composition and varying backbone lengths ($N_{\text{bb}} = 44\text{--}363$, see SI). To achieve consistent control over z , the targeted macromonomer/diluent feed ratios were verified by ^1H NMR prior to initiating the first block with **G3**. After reaching >99% conversion, the reaction mixtures were quenched by addition of excess ethyl vinyl ether. The block polymers were precipitated into methanol at -78°C , isolated by filtration, and dried under vacuum for >24 h. The first blocks and precipitated products were analyzed by NMR and size-exclusion chromatography (SEC), allowing determination of the molecular weights and therefore N_{bb} . These analyses indicated that our methodology produced well-defined, monodisperse ($D = 1.01\text{--}1.18$) graft block polymers.

Figure 2. *Top:* Scheme of **System I**, consisting of block polymer $(\text{PLA}^z\text{-}r\text{-DME}^{1-z})_n\text{-}b\text{-(PS}^z\text{-}r\text{-DBE}^{1-z})_n$ with variable total backbone degrees of polymerization ($N_{bb} = 2n$) and grafting densities (z). (a) Stacked 1D azimuthally averaged SAXS profiles for $z = 1$, indicating well-ordered lamellar morphologies. (b) Experimental data for the lamellar period (d^*) and N_{bb} (circles), as well as calculated power-law fits ($d^* \sim N_{bb}^\alpha$, lines). (c) Plot of the scaling exponents (α) as a function of z . A transition occurs around $z = 0.2$ (dotted line).

Self-assembly and the lamellar period. With these graft block polymers in hand, we studied their self-assembly to lamellar morphologies. The isolated polymers were thermally annealed at 140°C for 24 h under modest pressure (applied using binder clips). The samples were analyzed by synchrotron-source small-angle X-ray scattering (SAXS). Representative azimuthally averaged SAXS profiles corresponding to five samples with $z = 1$ are shown in Figure 2a. For all of the series investigated, the scattering patterns are consistent with well-ordered lamellar morphologies (see SI). Scanning electron microscope (SEM) images obtained for selected block polymers with

$N_{bb} \approx 200$ and $z = 1.00, 0.75, 0.50$, or 0.25 also indicate long-range-ordered lamellar structures (Figure 3).

We note that varying the grafting density also changes the chemical composition within each block (*i.e.*, by substituting **PLA** with **DME** and **PS** with **DBE**), potentially complicating the comparison of series with different z . In order to address the effects of varying the backbone chemistry, samples corresponding to loosely grafted individual first and second blocks – (**PLA**^{0.05}-*r*-**DME**^{0.95})₂₀₀ and (**PS**^{0.05}-*r*-**DBE**^{0.95})₂₀₀, respectively – were also prepared. These samples were annealed under the same conditions as the graft block polymers. No evidence of microphase separation was observed by SAXS (see SI), suggesting that each block behaves as a single component. In other words, the effective χ in each block between the backbone and side chains is negligible.

Figure 3. Scanning electron micrographs of graft block polymers with (a) $z = 1.00$, (PLA)₁₀₀-*b*-(PS)₁₀₀; (b) $z = 0.75$, (PLA^{0.75}-*r*-DME^{0.25})₁₁₀-*b*-(PS^{0.75}-*r*-DBE^{0.25})₁₁₀; (c) $z = 0.50$, (PLA^{0.5}-*r*-DME^{0.5})₁₀₄-*b*-(PS^{0.5}-*r*-DBE^{0.5})₁₀₄; and (d) $z = 0.25$, (PLA^{0.25}-*r*-DME^{0.75})₁₁₂-*b*-(PS^{0.25}-*r*-DBE^{0.75})₁₁₂.

For all graft block polymers, the lamellar periods (d^*) were determined by indexing the raw SAXS data. Figure 2b shows plots of d^* versus N_{bb} . The scaling relationships for each series were calculated using a least-square power-law fitting function in *Igor*. To gain additional insight into the scaling behavior, the determined scaling exponents α were plotted as a function of z (Figure 2c). For the $z = 1$ series, the large magnitude of α (0.858) is consistent with previously reported values for symmetric PLA-*b*-PS bottlebrush block polymers ($\alpha = 0.8$ – 0.9).^{21-25,53} At the other extreme, the $z = 0$ series exhibits an α value of 0.685, very close to the theoretical value ($\alpha = 2/3$) for strongly segregated symmetric linear diblock polymers.¹¹ The variable- z series ($z = 0.75, 0.50, 0.35, 0.25, 0.20, 0.15, 0.05$) constitute intermediate regimes bridging the two extremes. Comparing all series, the scaling exponents decrease monotonically with decreasing z . However, while α modestly decreases from 0.858 ($z = 1.00$) to 0.779 ($z = 0.20$), it then sharply decreases with decreasing z to 0.685 ($z = 0$). Collectively, these trends suggest changes in the backbone conformation with decreasing grafting density. Consistent with recent experimental and theoretical reports, at a certain critical z the conformational regime may transition from densely grafted brushes to loosely grafted brushes or combs.^{54,55} These changes significantly impact the physical properties of graft homopolymers, such as the plateau modulus and extensibility. However, the effects of grafting density on block polymer phase behavior are unexplored to date. In the final section of this report, we will propose a model for the observed scaling behavior.

System II: Same diluent for both blocks. The potential consequences of altering χ within each block were dismissed, and individual blocks can be treated as single components. However, varying the grafting density in **System I** may also affect the effective χ between blocks. Changing χ would influence d^* and potentially complicate the interpretations of the observed scaling trends. For symmetric linear diblock polymers, d^* exhibits a weak dependence on χ in the strongly

segregated regime ($d^* \sim \chi^{1/6}$) and is independent of χ in the weakly segregated regime. In the mean-field Flory-Huggins lattice model, χ is determined by the number of nearest neighbor contacts per monomer. In our materials, since the number ratio of diluents to side chain monomers (*i.e.*, either lactide or styrene repeats) is very small, the diluents are not expected to significantly affect χ . We anticipate that the large size disparity between macromonomers and diluents should make polymer architecture the primary factor responsible for the observed trends.

Figure 4. $(\text{PLA}^z\text{-}r\text{-DBE}^{1-z})_n\text{-}b\text{-(PS}^z\text{-}r\text{-DBE}^{1-z})_n$ of variable backbone degrees of polymerization ($N_{\text{bb}} = 2n = 82\text{--}533$) and grafting densities ($z = 0.75, 0.50, 0.35, 0.25, 0.15, 0.12, 0.06$, and 0.05).

To examine this hypothesis, we prepared **System II** in which the same diluent (**DBE**) was employed to vary z in both blocks (Figure 4). The lowest- z extreme ($z = 0$) in **System II** is the homopolymer **(DBE)_n**, which does not microphase separate. Macromonomers **PLA** ($M_n = 3030$ g/mol) and **PS** ($M_n = 3800$ g/mol) of similar molecular weights as those in **System I** were used. The determined reactivity ratios ($r_{\text{PLA}} = 1.04$, $r_{\text{DBE}} = 0.89$; $r_{\text{PS}} = 0.83$, $r_{\text{DBE}} = 1.16$) indicated random copolymerization within each block and therefore uniform grafting density. As for **System I**,

polymers of general formula $(\text{PLA}^z\text{-}r\text{-DBE}^{1-z})_n\text{-}b\text{-}(\text{PS}^z\text{-}r\text{-DBE}^{1-z})_n$ were prepared ($N_{\text{bb}} = 2n = 82\text{--}533$; $z = 0.75, 0.50, 0.35, 0.25, 0.15, 0.12, 0.06, 0.05$). The isolated monodisperse ($\mathcal{D} = 1.02\text{--}1.19$) copolymers were characterized by NMR and SEC.

The samples were thermally annealed under the same conditions as **System I**. All of the polymers in **System II** self-assembled into well-ordered lamellae as evidenced by SAXS (see SI). Azimuthally averaged 1D SAXS plots obtained for the $z = 0.75$ series are shown in Figure 5a as representative examples. Figure 5b shows the power-law fitting plots (d^* versus N_{bb}) for each series. The α values in **System II** are uniformly smaller compared to their counterparts of the same grafting density in **System I**. This observation could be attributed to the larger changes in χ between blocks upon decreasing z . The $z = 0.05$ series displays an α value of 0.515, approaching the theoretical value in the weak segregation limit ($\alpha = 1/2$).^{11,12} Comparing Figures 2c and 5c suggests that the different d^* and α values are likely due to different changes in χ . The linear diblock polymer $(\text{DME})_n\text{-}b\text{-}(\text{DBE})_n$, which is exactly the $z = 0$ series in **System I**, is itself strongly segregated, whereas the $z = 0$ series in **System II** is the homopolymer $(\text{DBE})_n$. However, we note that the transition between regions of shallow and steep decreases in α with decreasing z occurs at nearly the same z in both systems ($z \approx 0.2$), suggesting that such transition is intrinsically related to polymer architecture rather than segregation strengths.

Significance of the determined scaling relationships. Our experiments shed light on how grafting density affects the scaling of the lamellar period with the total backbone degree of polymerization. Understanding these scaling relationships expands the parameter space for materials design. Materials with controlled length scales are desired for many applications. For example, ultra-large d^* values are required by photonic crystals in order to access the visible spectrum. In general, linear polymers are prohibitively challenging to synthesize and process at

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3 sufficiently high molecular weights. Meanwhile, bottlebrush block polymers are attractive
4 building blocks due to their reduced chain entanglement and steep increase in d^* with molecular
5 weight. However, synthesizing fully grafted, ultra-high-molecular-weight bottlebrush block
6 polymers can be challenging and expensive. In grafting-through strategies, the concentrations of
7 reactive chain ends are inherently low, and the side chains are typically synthesized by costly
8 metal-mediated controlled polymerizations. Through grafting-through copolymerization however,
9 N_{bb} can be readily increased by introducing small-molecule diluents that can be synthesized on
10 large scales from readily available precursors.
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13 The ability to simultaneously tune the grafting density and backbone length provides an
14 additional tool for designing materials with desired length scales. For example, according to the
15 determined scaling relationship for fully grafted bottlebrush block polymers ($z = 1.00$, $d^* = 1.033$
16 $\times N_{bb}^{0.858}$), a polymer with $N_{bb} = 100$ should self-assemble to lamellae with $d^* = 53.6$ nm. In
17 **System I**, a 50% grafted block polymer ($z = 0.50$, $d^* = 0.926 \times N_{bb}^{0.815}$) with the same number of
18 side chains has $N_{bb} = 200$ and should self-assemble to lamellae with $d^* = 69.5$ nm. In other words,
19 decreasing the grafting density ($z = 1.00$ to 0.50) while maintaining the same number of side chains
20 results in a large increase in d^* (30%) at the expense of only a small increase in total molecular
21 weight (7%). The modest increase in M is highly advantageous for processing these materials since
22 the zero-shear viscosity scales with M ($\eta_0 \sim M^\alpha$). Below the onset of entanglements at a critical
23 molecular weight M_c , $\alpha = 1$, whereas above M_c , $\alpha = 3.4$. The influence of grafting density on
24 rheological properties is currently being studied by our group and others.
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Figure 5. *Top:* Scheme of **System II**, consisting of block polymer $(\text{PLA}^z\text{-}r\text{-}\text{DBE}^{1-z})_n\text{-}b\text{-(PS}^z\text{-}r\text{-}\text{DBE}^{1-z})_n$ with variable total backbone degrees of polymerization ($N_{bb} = 2n$) and grafting densities (z). (a) Stacked 1D azimuthally averaged SAXS profiles for $z = 0.75$, indicating well-ordered lamellar morphologies. (b) Experimental data for the lamellar period (d^*) and N_{bb} (circles), as well as calculated power-law fits ($d^* \sim N_{bb}^\alpha$, lines). (c) Plot of the scaling exponents (α) as a function of z . A transition occurs around $z = 0.2$ (dotted line). Note that in (b) and (c), unfilled circles indicate data for **System I** ($z = 1.00$), in which the side chain molecular weights are slightly higher.

We further highlight the significance of grafting density effects on the scaling of the lamellar period by predicting the required N_{bb} to reach an arbitrary value of $d^* = 200$ nm (Figure 6). Such a large d^* is desired for photonic applications. At the same z , N_{bb} required to reach $d^* = 200$ is larger for block polymers in **System II** than in **System I** as a result of differences in segregation strengths. In both systems, the predicted N_{bb} values exponentially increase with

decreasing z below the observed transition ($z < 0.20$). In the linear block polymer limit ($z = 0$, **System I**), the required N to reach $d^* = 200$ nm is close to 4000. Such high-molecular-weight linear polymers are extremely challenging to synthesize, and as a result there are very few examples of linear block polymers that can self-assemble to visible-light-reflecting photonic crystals.⁵⁶ Existing examples are typically limited by low conversion and inability to process the materials from the melt. In contrast, a 50% grafted block polymer should only require $N_{bb} \approx 730$. Manipulating the grafting density through copolymerization therefore constitutes a promising strategy to overcome limitations associated with both synthesis and processing.

Figure 6. Plots of predicted N_{bb} required to access $d^* = 200$ nm as a function of grafting density (z) for (a) **System I** and (b) **System II**.

Interpretation of the scaling trends. We derive a potential model in order to relate the observed changes in α with grafting density (z) to the conformations of the graft polymer backbone and side chains. Key experimental results to capture include (1) the monotonic decrease in α with

z (Figures 2c and 5c), (2) the apparent transition between shallow and steep decreases in α at a critical $z_c = 0.2$, and (3) potential segregation effects that emerge at low z . Comparison of two systems – one in which all series ($z \geq 0$) are in the strongly segregated limit (SSL) (**System I**) and one that bridges the strongly and weakly segregated limits (WSL) (**System II**) – suggests that architecture effects, not segregation effects, are primarily responsible for the observed trends. We will begin by framing our results in the context of existing theory for the self-assembly of diblock polymers, then propose a functional form for the observed relationship between z and d^* , *i.e.*, $d^* \sim N_{bb}^{f(z)}$. We note that, in part due to the long-standing challenges associated with synthesizing well-defined graft polymers, there is not currently a theoretical or experimental consensus detailing the effects of grafting density on block polymer self-assembly.

The scaling of the lamellar period (d^*) is well-understood in the case of symmetric linear diblock polymers.^{11,12,57} The magnitude of d^* is determined by the balance between the elastic energy (F_{stretch}), which resists chain stretching, and the interfacial energy (F_{int}), which resists expansion of block junctions along the domain interfaces. The stretching free energy per polymer chain is inversely proportional to the mean-square end-to-end distance, $\langle R^2 \rangle$:

$$\frac{F_{\text{stretch}}}{kT} \sim \frac{d^{*2}}{\langle R^2 \rangle} \quad (4)$$

When the chain is flexible, the mean-square end-to-end distance is given by $\langle R^2 \rangle = a_0^2 N_{bb}$, where a_0 is the statistical segment length and N_{bb} is the backbone degree of polymerization. (Note that in the case of linear polymers, N_{bb} is identical to the *total* degree of polymerization.) The interfacial energy per polymer chain is

$$\frac{F_{\text{int}}}{kT} \sim \gamma A \quad (5)$$

where γ is the surface tension and A is the area per chain. These parameters can be approximated by $\gamma = \chi^{\frac{1}{2}} a_0^{-2}$ and $A \sim N_{\text{bb}} a_0^3 / d^*$, leading to the following expression:

$$\frac{F_{\text{int}}}{kT} \sim \frac{N_{\text{bb}} a_0 \chi^{\frac{1}{2}}}{d^*} \quad (6)$$

In the SSL, the elastic energy and interfacial energy are balanced ($F_{\text{stretch}} = F_{\text{int}}$), and thus we obtain

$$d^* \sim \chi^{\frac{1}{6}} N^{\frac{1}{3}} [\langle R^2 \rangle]^{\frac{1}{3}} \sim a_0 \chi^{\frac{1}{6}} N_{\text{bb}}^{\frac{2}{3}} \quad (7)$$

In the WSL, the chains do not significantly stretch at the interface because χ is small, and thus F_{int} is effectively negligible. Therefore,

$$d^* \sim [\langle R^2 \rangle]^{\frac{1}{2}} \sim a_0 N_{\text{bb}}^{\frac{1}{2}} \quad (8)$$

Collectively, following Eqs. 7 and 8, the d^* scaling relationship for diblock polymers has the general form

$$d^* \sim a_0 N_{\text{bb}}^{\alpha} \quad (9)$$

For flexible linear diblock polymers, typically $1/2 \leq \alpha \leq 2/3$. In contrast, when the polymer is semi-flexible, the same general form applies but the scaling exponent α is larger.^{58,59} Bottlebrush diblock polymers typically exhibit α close to 0.9, reflecting the extended backbone conformations due to the sterically demanding architecture.^{23,24,32} We note that, in the limit of extremely long backbones, when the persistence length and cross-sectional diameter are much shorter than the contour length of the brush, the chain should become flexible and α should approach $2/3$.^{25,60} In the current study however, the graft polymers exclusively reside in the regime in which the backbone persistence length (l_p) is not negligible compared to N_{bb} .

For non-flexible polymers, the mean-square end-to-end distance can be written as

$$\langle R^2 \rangle = a_0^2 C_{\infty} N_{\text{bb}} \quad (10)$$

by adopting Flory's characteristic ratio, $C_{\infty} = 2l_p/a_0$. Therefore,

$$\langle R^2 \rangle = 2a_0 l_p N_{bb} \quad (11)$$

For bottlebrush polymers, l_p is a function of the side chain degree of polymerization (N_{sc}) and z .^{55,61} l_p is also anticipated to be a function of N_{bb} by theory and simulations,^{54,62} but the functional form of this relationship is currently a matter of some debate. We will assume that C_∞ is a function of N_{bb} and z in order to study how the backbone stiffness affects d^* .

Two boundary conditions of this function are known. First, when $z = 0$, $C_\infty = 1$ by definition since the backbone is identical to a flexible linear polymer. Second, in the opposite limit, when $z = 1$, C_∞ should approach N_{bb} . To satisfy these conditions, we write the following power function describing the relationship between C_∞ and N_{bb} :

$$C_\infty = N_{bb}^{mz+b} \quad (12)$$

We now insert Eq. 12 into Eq. 10, then rewrite the expressions for d^* in the SSL (Eq. 7) and WSL (Eq. 8) in terms of C_∞ :

$$d^* \sim \begin{cases} a_0 \chi^{\frac{1}{6}} C_\infty^{\frac{1}{3}} N_{bb}^{\frac{2}{3}} & \text{SSL} \\ a_0 C_\infty^{\frac{1}{2}} N_{bb}^{\frac{1}{2}} & \text{WSL} \end{cases} \quad (13)$$

Therefore, the experimentally observed scaling exponents α can be written as follows:

$$\alpha = \begin{cases} \frac{mz+b+2}{3} & \text{SSL} \\ \frac{mz+b+1}{2} & \text{WSL} \end{cases} \quad (14)$$

We now apply Eq. 14 to **Systems I** and **II** in order to evaluate how C_∞ , as a proxy for the backbone stiffness, changes with z . In **System I**, different diluents (**DME** and **DBE**) are used to vary z in each block. The linear diblock polymer **DME-*b*-DBE** exhibits $\alpha = 0.688 \approx 2/3$. This result suggests that, even in the $z = 0$ limit, the block polymers in **System I** are strongly segregated. Since α should only increase with z , all series in **System I** are expected to be in the SSL. Figure 7a shows

the lines of best fit for experimentally determined values of α and z . Two regions were identified, diverging at a critical grafting density $z_{c,I}$: (1) when $z < 0.2$, α steeply decreases with decreasing z ; (2) when $z > 0.2$, α slightly decreases with decreasing z . In the first region, $\alpha = 0.46z + 0.68$; in the second region, $\alpha = 0.091z + 0.77$. The lines of best fit intersect at $z_{c,I} = 0.23$. We obtain the following expressions for C_∞ :

$$C_\infty = \begin{cases} N_{bb}^{1.39z} & z < 0.23 \\ N_{bb}^{0.27z+0.30} & z > 0.23 \end{cases} \quad (15)$$

Introducing Eq. 15 into Eq. 10 enables calculations of the normalized root-mean-square end-to-end distances ($\sqrt{\langle R^2 \rangle}/a_0$) as a function of z (Figure 7a). The transition in $\sqrt{\langle R^2 \rangle}/a_0$ occurs near $z_{c,I}$: $z = 0.27$.

Unlike **System I**, **System II** uses the same diluent (**DBE**) for both blocks. The $z = 0$ limit constitutes a linear homopolymer rather than a diblock polymer, and therefore the segregation behavior and chain stretching at the domain interface differ between **Systems I** and **II**. Applying the same analysis for **System II**, when the grafting density is low ($z < 0.2$) we obtain $\alpha = 1.44z + 0.50$ (Figure 7b). In this region, the block polymers experience intermediate to weak segregation ($\alpha < 2/3$). Reflecting the boundary condition $C_\infty = 1$ at $z = 0$, the y-intercept was fixed at $1/2$. Therefore, applying Eq. 14 in the WSL, $m = 2.87$ and $b = 0$. By comparison to **System I** and literature results, we expect the series to experience strong segregation at a certain z . We will assume that, at least when $z > 0.2$, the block polymers are in the SSL. Therefore, $\alpha = 0.15z + 0.71$ suggests $m = 0.46$, $b = 0.12$. The lines of best fit intersect at $z_{c,II} = 0.16$. From these results, for **System II** we obtain the following expression for C_∞ :

$$C_\infty = \begin{cases} N_{bb}^{2.87z} & z < 0.16 \\ N_{bb}^{0.46z+0.12} & z > 0.16 \end{cases} \quad (16)$$

Figure 7b (bottom) shows the values of $\sqrt{\langle R^2 \rangle}/a_0$ calculated for **System II** per Eq. 16. Surprisingly, $\sqrt{\langle R^2 \rangle}/a_0$ exhibits an apparent transition at $z = 0.05$, much lower than the value $z_{c,II} = 0.16$ identified by fitting the experimental data (Figure 7b, top). In contrast, for **System I** the transitions in α and $\sqrt{\langle R^2 \rangle}/a_0$ occur at approximately the same z (Figure 7a). Since $\sqrt{\langle R^2 \rangle}/a_0$ is obtained from fitting α in two regions (diverging at a critical z_c and assuming either weak or strong segregation), the transitions should occur at the same z if the proposed model accurately describes the entire z range. The observed mismatch suggests that our model does not reflect all factors affecting d^* in the transition region. The preceding discussions have focused on the backbone stiffness. However, the potential contributions of χ and side chain conformations should also be considered.

Figure 7. Analysis of scaling trends with grafting density (z) for (a) **System I** and (b) **System II**. (top) Experimentally determined values and lines of best fit for the scaling exponent (α) versus z . The lines intersect at a critical z_c , associated with a transition in the backbone stiffness. In (b), the

unfilled circle ($z = 1.00$) indicates data for **System I**. (*bottom*) Calculated root-mean-square end-to-end distances, normalized by the backbone statistical segment length ($\sqrt{\langle R^2 \rangle}/a_0$), fixing $N_{bb} = 100$.

Figure 7 indicates that changes in C_∞ alone do not fully capture the scaling of the lamellar period. Changes in the segregation strength that emerge with decreasing z are likely also significant. In **System I**, the diluents are different and the polymers are already stretched at $z = 0$ (inferred based on $\alpha > 2/3$). Since the backbones are already stretched, increasing z may not significantly affect χ between the two grafted blocks or backbone stretching. A high grafting density (large z_c) may be required to further stretch the chains. In **System II** however, the $z = 0$ limit describes linear homopolymers, which are expected to adopt unperturbed conformations. Therefore, the onset of backbone and side chain stretching should occur at a lower z_c . The effects of segregation, as well as the precise location of the transition between SSL and WSL with z , are important factors to consider.

To conclude our interpretation of the scaling relationships, we address the potential role of the side chains in the experimentally observed transition at $z_c \approx 0.20$. Our analysis is consistent with C_∞ changing abruptly at z_c . We note that, for **System I**, all series ($0 \leq z \leq 1$) are in the SSL. Steric repulsion between the side chains is expected to be the primary factor responsible for increasing C_∞ . The location of the transition z_c is therefore expected to be related to the onset of side chain overlap. The radius of gyration of a side chain is

$$R_{g,sc} = a_{sc} (N_{sc}/6)^{\frac{1}{2}} \quad (17)$$

where a_{sc} is the statistical segment length of the side chain. In order for the side chains to retain their unperturbed conformations, the contour length of a section of backbone separating adjacent

side chains (L_g) should be larger than $2R_{g,sc}$. As z increases, the side chains are expected to stretch to accommodate tethering at shorter L_g .⁶¹ Consistent with a convention employed by previous theories and experiments for bottlebrush polymers,²⁵ we assume that the contour length per polynorbornene backbone segment is constant ($L_s = 0.62$ nm). The number of backbone segments between adjacent grafting points (inclusive) is provided by $1/z$, and L_g follows:

$$L_g = \frac{L_s}{z} \quad (18)$$

When $L_g > 2R_{g,sc}$, the backbone is expected to behave as a flexible Gaussian chain. When $L_g < 2R_{g,sc}$, the backbone is expected to stretch, ultimately leading to wormlike chain conformations at sufficiently high z . The stiffness of the brush is expected to increase when two neighboring grafts contact each other in the limiting range of the torsional angle. We define z_s as the grafting density at the onset of backbone stretching due to torsional limitations ($L_g = 2R_{g,sc}$):

$$z_s \equiv \frac{L_s}{2a_{sc} (N_{sc}/6)^{\frac{1}{2}}} \quad (19)$$

As an approximation, we estimate that the transition in the brush conformation responsible for the transition in α occurs when $z = z_s$. We note that stretching of the side chains at $z > z_s$ may not permit this simple approximation, since stretching of the graft polymer backbone and side chains should compete to balance conformational entropy. We further assume $N_{sc} = 36$ and $L_s \approx a_{sc}$, producing $z_s = 0.20$. For both **Systems I** and **II**, the experimentally observed transition in α occurs at $z_c \approx z_s$ ($z_{c,I} = 0.23$, $z_{c,II} = 0.16$). This observation suggests that the steep increase in α at small z is mainly due to the stretching of the backbone, whereas the modest increase in α at high z is mainly due to the increasing torsional angle demanded by decreasing L_g .

These results collectively suggest that changes in the end-to-end distance $\langle R^2 \rangle$ are primarily responsible for the increase in α with increasing z . $\langle R^2 \rangle$ may increase due to a

combination of backbone stretching, torsional limitations, and χ effects. $\langle R^2 \rangle$ exhibits two regimes in terms of z dependence, potentially corresponding to a transition between loose and densely grafted brushes.^{54,55} In our model, we propose functional forms for (1) the relationship between backbone stiffness and backbone length ($C_\infty \sim N_{bb}^{f(z)}$) and (2) the relationship between the lamellar period scaling exponent and grafting density ($\alpha \sim mz + b$). We anticipate that the materials and framework outlined herein should stimulate additional theories and experiments.

CONCLUSIONS

The self-assembly of block polymers enables diverse practical applications. We herein provide experimental evidence that quantitatively correlates grafting density with scaling of the lamellar period. Through the analyses of well-defined graft block polymer assemblies, we show that the scaling exponent undergoes a sharp transition at $z \approx 0.20$. The observed transition is attributed to different conformational regimes dictated by backbone chain conformations. We envisage that the determined scaling relationships for various grafting density series could be exploited to guide material design.

MATERIALS AND METHODS

General considerations. Norbornene macromonomers **PS**⁶³ and **PLA**²³ were prepared according to previously reported precedures. Norbornene diluents **DME**⁶⁴ and **DBE**⁶⁵ were prepared by Diels-Alder reactions according to previously reported procedures. Grubbs' second-generation catalyst $[(H_2IMes)(PCy_3)(Cl)_2Ru=CHPh]$ was provided by *Materia*, and **G3** was prepared according to the reported procedure.⁶⁶ CH_2Cl_2 was dried by passing through an activated

alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and used as received.

NMR, SEC, SEM, and SAXS characterizations. Ambient temperature NMR spectra were recorded on a Varian 300 MHz, 400 MHz, or 500 MHz NMR spectrometer. Chemical shifts (δ) were given in ppm and referenced against residual solvent signals (^1H , ^{13}C). SEC data were collected using two Agilent PLgel MIXED-B 300×7.5 mm columns with $10 \mu\text{m}$ beads, connected to an Agilent 1260 Series pump, a Wyatt 18-angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. The mobile phase was THF. Online determination of dn/dc assumed 100% mass elution under the peak of interest. (Further details about SEC can be found in the SI.) Samples were prepared for SEM by fracturing films supported on glass to expose a cross-section, staining over ruthenium tetroxide vapors for 5 minutes, then coating with 5 nm Pd/Pt. SEM images were taken on a ZEISS 1550 VP Field Emission SEM. SAXS data were collected at beamline 12-ID at Argonne National Laboratory's Advanced Photon Source. The samples were probed using 12 keV ($1.033 \text{ \AA}$) X-rays, and the sample-to-detector distance was calibrated using a silver behenate standard. The beam was collimated using two sets of slits and a pinhole was used to remove parasitic scattering. The beamwidth was approximately $200\text{--}300 \mu\text{m}$ horizontally and $50 \mu\text{m}$ vertically.

ASSOCIATED CONTENT

Supporting Information. Lamellar scaling equations, SEC traces, SAXS images.

These materials are available free of charge *via* the Internet at <http://pubs.acs.org>.

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