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Bottlebrush Polymer Synthesis by Ring-Opening Metathesis Polymerization: The Significance of the Anchor Group

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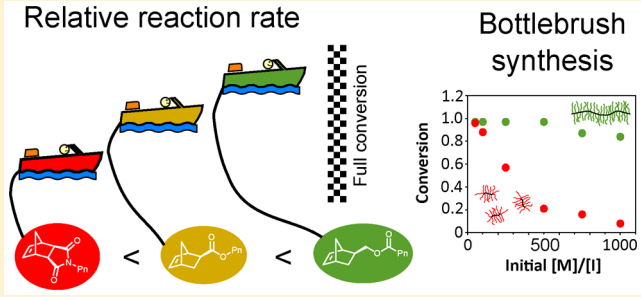
Supporting Information

ABSTRACT: Control over bottlebrush polymer synthesis by ring-opening metathesis polymerization (ROMP) of macromonomers (MMs) is highly dependent on the competition between the kinetics of the polymerization and the lifetime of the catalyst. We evaluated the effect of anchor group chemistry—the configuration of atoms linking the polymer to a polymerizable norbornene—on the kinetics of ROMP of polystyrene and poly(lactic acid) MMs initiated by $(H_2IMes)(pyr)_2(Cl)_2Ru{=}CHPh$ (Grubbs third generation catalyst). We observed a variance in the rate of propagation of >4-fold between similar MMs with different anchor groups. This phenomenon was conserved across all MMs tested, regardless of solvent, molecular weight (MW), or repeat unit identity. The observed >4-fold difference in propagation rate had a dramatic effect on the maximum obtainable backbone degree of polymerization, with slower propagating MMs reducing the maximum bottlebrush MW by an order of magnitude (from ~10^6 to ~10^5 Da). A chelation mechanism was initially proposed to explain the observed anchor group effect, but experimental and computational studies indicated that the rate differences likely resulted from a combination of varying steric demands and electronic structure among the different anchor groups. The addition of trifluoroacetic acid to the ROMP reaction substantially increased the propagation rate for all anchor groups tested, likely due to scavenging of the pyridine ligands. Based on these data, rational selection of the anchor group is critical to achieve high MM conversion and to prepare pure, high MW bottlebrush polymers by ROMP grafting-through.



INTRODUCTION

The study of bottlebrush polymers has gained momentum in recent years due to the unique architecture and physical properties of this polymer topology.[1,2] Comprised of numerous polymeric side chains densely grafted to a polymer backbone, the highly branched nature of bottlebrush polymers results in steric repulsion between neighboring polymer chains, forcing these macromolecules to adopt a chain-extended conformation.[3,4] Bottlebrush polymers differ from their linear analogs in their size, shape persistence, cylindrical nanostructure, and their inability to interact through chain entanglement—properties that are highly dependent on the molecular weight (MW) of the pendant side chains as well as the backbone degree of polymerization (DP).[5,6] Consequently, bottlebrush polymers have become increasingly relevant in applications such as rheology modifiers,[7] supersoft elastomers,[8] photonic crystals,[9] antifouling coatings,[10] the in vivo delivery of therapeutic agents,[11,12] and as promising substrates in lithographic printing.[13,14]

Despite recent progress, bottlebrush polymers with controllable MWs, high side-chain and backbone DPs, narrow molecular weight distributions, and uniform grafting densities remain challenging synthetic targets. There are a number of approaches toward the synthesis of these macromolecules, and each has its advantages and shortcomings. The grafting-through approach involves the polymerization of macromonomers (MMs) (polymers that contain a polymerizable chain end) to form a "perfectly grafted" bottlebrush polymer. Bottlebrush polymers prepared using this technique possess polymeric side chains of known and uniform MW, as MMs are synthesized prior to the grafting step. Additionally, grafting-through allows for 100% grafting density, unlike other methods.[15] However, this technique is often limited to low DPs for the bottlebrush polymer backbone due to the relatively low concentration of polymerizable end groups and steric congestion around the propagating site caused by the interaction of two polymeric species.[16]

Many reports on the grafting-through strategy employ ring-opening metathesis polymerization (ROMP) of MMs containing norbornene end groups.[17−26] During ROMP grafting-through, highly active olefin metathesis catalysts mediate the polymerization of MMs functionalized with strained terminal norbornenes to afford narrow dispersity bottlebrush polymers

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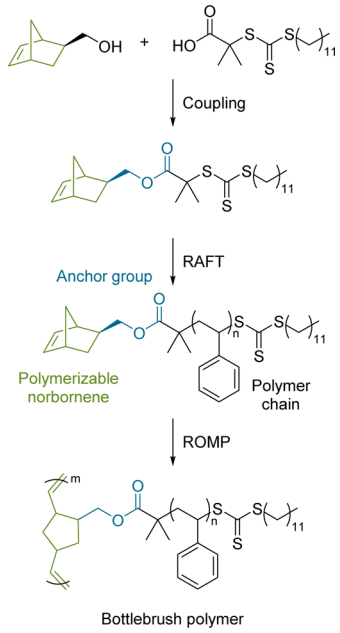
with a great degree of control over backbone and side-chain MW.[27] However, while some very high MW bottlebrush polymers have been prepared by ROMP grafting-through,[28−30] low backbone DPs or side-chain MWs are more commonly reported. In fact, some reports indicate that an inherent backbone DP ceiling exists for specific MMs under their tested conditions.[31−33] Intuitively, the maximum DP that is obtainable in ROMP grafting-through is limited by the following (among other factors): (1) the rate of propagation of the polymerization; (2) the limited lifetime of the active catalytic species (a form of termination in ROMP). Therefore, complete conversion of an MM to a bottlebrush polymer can be obtained with rapidly propagating MMs, while incomplete conversions result from MMs that propagate slowly, such that the time scale of the polymerization exceeds the lifetime of the catalyst. Incomplete conversion as the result of catalyst deactivation is particularly problematic in grafting-through syntheses of bottlebrush polymers using ROMP because it leads to a broadening of the molecular weight distribution and contaminates the bottlebrush polymer sample with residual MM impurities that can be difficult to remove.

In our laboratory we have often observed widely different MM conversions and ultimate molecular weights despite employing the same ROMP catalyst, the same solvent, the same type of repeat unit in the MM, and MMs of similar MWs. Similar discrepancies appear throughout the literature. Considering these puzzling results, we sought to understand why some MMs undergo ROMP quickly to high conversion and high DP while nearly identical MMs undergo relatively slower propagation, achieve a lower maximum conversion, and have a lower backbone DP as a result. The three-dimensional shape of bottlebrush polymers (i.e., cylindrical or globular) depends largely on the backbone DP and ultimately determines their possible applications.[5,30,34] Therefore, measuring and controlling the factors that affect the rate of MM polymerization (and correspondingly, the molecular weight of the bottlebrush polymer) will enable access to a wider variety of well-defined bottlebrush polymers via the grafting-through approach.

MMs functionalized with a norbornene derivative on their chain terminus are commonly prepared by esterification or imidization of norbornene carboxylic acid,[29] norbornenol,[18] or norbornene anhydride[27] derivatives (Scheme 1). These reactions represent convenient routes to attach the polymer unit to the polymerizable functionality and are ubiquitous to ROMP grafting-through regardless of the method of MM synthesis. Ultimately, these reactions leave a carbonyl near the Ru center in the propagating alkylidene species. The proximity of a carbonyl to the metal center influences the activity of the ruthenium carbene complex, as stable Ru chelates may sequester the catalyst in an unproductive form.[35−37] In particular, a significant retardation in the rate of propagation during ROMP of small molecule norbornene monomers using $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (Grubbs' first generation catalyst) has been demonstrated through a proposed chelation interaction between the carbonyl oxygen atom of the ring-opened monomers and the metal center.[38] In our efforts to prepare bottlebrush polymers by ROMP grafting-through using olefin metathesis catalyst $(H_2IMes)(pyr)_2(Cl)_2Ru{=}CHPh$ (**G3**), we have noticed a similar variance in the rate of propagation dependent on the chemical structure of the anchor group—the atoms connecting the polymer side chain to the polymerizable group. We imagined that the anchor group might be a leading cause for the observed variability in bottlebrush polymer synthesis by ROMP. Based on reported results, as well as our own observations, we initially hypothesized that an interaction between the carbonyl oxygen in the anchor group and the Ru center in the propagating alkylidene could compete with the binding of an incoming MM, thereby decreasing the rate of propagation. In this contribution, we investigate the effect of the anchor group on the rate of propagation, the MM conversion, and the maximum obtainable DP during ROMP grafting-through polymerization.

Scheme 1. Typical Synthesis of a Bottlebrush Polymer by ROMP Grafting-through



RESULTS AND DISCUSSION

To investigate the proposed anchor group effect, we prepared polystyrene MMs with three different moieties anchoring the polymer unit to the polymerizable norbornene chain end. MMs are named following the general scheme $\mathbf{XP}_y$ where X = anchor group **1**, **2**, or **3** (Figure 1A); P = monomer repeat unit, styrene (**S**), or lactide (**L**); and y = number-average molecular weight (M_n) of the MM (therefore, $\mathbf{3S}_{3k}$ indicates anchor group **3** (imide), with an attached polystyrene chain of 3 kDa). These anchor groups were chosen because they are widely used and provide varying degrees of proximity of the ester or imide carbonyl to the Ru center, with the norbornene imide and norbornene carboxylic acid derived groups placing the carbonyl in position to chelate the metal center via the formation of a six-membered ring. Stelzer and co-workers observed a retardation effect due to the existence of six-membered ring chelates in similarly functionalized monomers.[38] Therefore, we theorized that MMs of the type $\mathbf{1P}_y$, whose carbonyl group cannot chelate to the Ru center via formation of a six-memberd ring, should propagate more rapidly than MMs of type $\mathbf{2P}_y$ and $\mathbf{3P}_y$, which can chelate via a six-membered ring. Additionally, MMs of types $\mathbf{1P}_y$ and $\mathbf{2P}_y$ are monosubstituted with respect to the norbornene ring system, leading to the formation of two possible regioisomers for the propagating alkylidene. In the case of MM $\mathbf{2P}_y$, only one of the two regioisomers would have the potential for six-membered chelate formation. Based on these qualifications, we envisioned that MMs prepared using the

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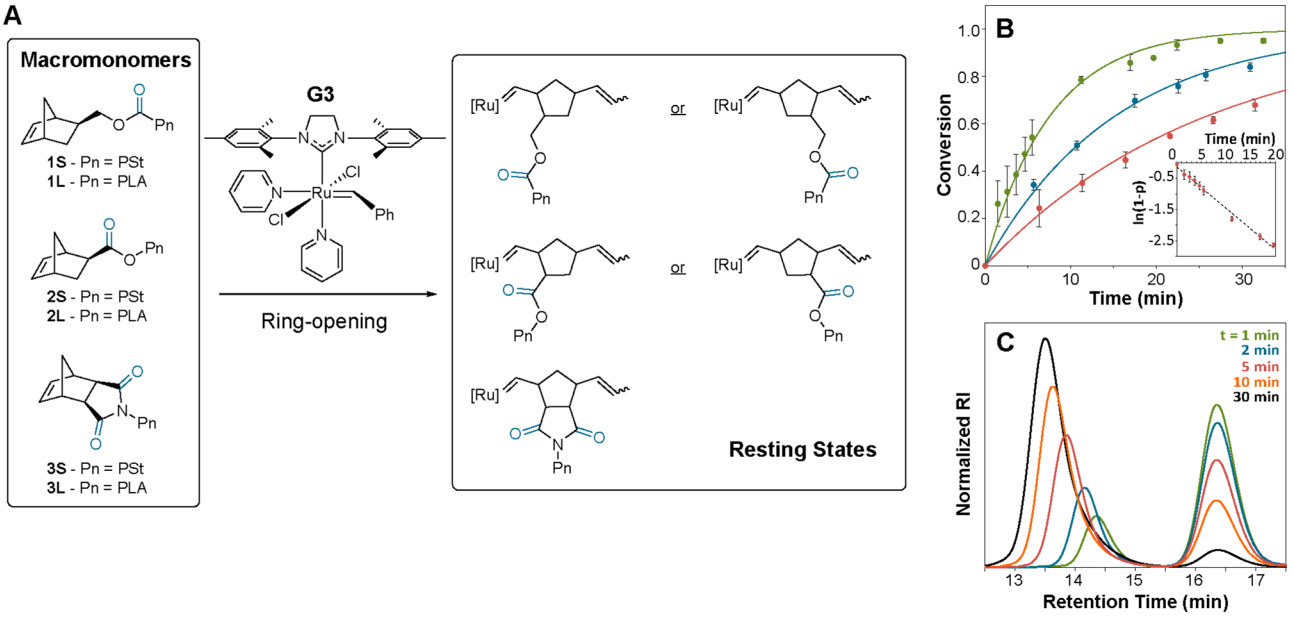

Figure 1. (A) Structures of propagating alkylidenes for various MMs highlighting (i) the potential for chelation between the carbonyl oxygen of the anchor group and the Ru center, and (ii) regioisomers that are unlikely to form chelates. (B) Kinetic analyses of ROMP of MMs with different anchor groups: representative kinetic plot of in situ NMR experiments using polystyrene MMs of $M_n \approx 3000$ Da with an [MM]/[**G3**] ratio of 100 at 50 mg/mL (green circles = $\mathbf{1S_{3k}}$, blue circles = $\mathbf{2S_{5k}}$, red circles = $\mathbf{3S_{3k}}$). Solid lines represent fits of each data set generated using experimentally determined k_p values based on the equation $p = 1 - e^{(-k_p t)}$. (B, inset) Representative log plot for in situ NMR kinetic analysis of MM $\mathbf{1S_{3k}}$. (C) Representative SEC traces of the kinetic study of MM $\mathbf{1S_{3k}}$. The peaks at longer retention times (ca. 16.5 min) correspond to residual MM.

Table 1. Summary of ROMP Kinetic Analysis of MMs[a]

	measured by NMR			measured by SEC[i]					
MM name	k_p (10^{-3} L * mol^{-1} * s^{-1})[b]	$t_{1/2}$ (s)[c]	% conv[d]	k_p (10^{-3} L * mol^{-1} * s^{-1})[e]	$t_{1/2}$ (s)[c]	% conv[f]	BB M_n (kDa)[g]	BB $M_{n,expected}$ (kDa)[h]	BB Đ[g]
$\mathbf{1S_{3k}}$	11 ± 2	68 ± 20	>99	8.0	87	95	280	280	1.01
$\mathbf{2S_{3k}}$	3.3 ± 0.3	210 ± 20	98	3.6	190	89	260	280	1.01
$\mathbf{3S_{3k}}$	1.6 ± 0.2	450 ± 80	91	1.6	430	87	250	260	1.03
$\mathbf{1S_{5k}}$	2.9 ± 0.4	250 ± 40	>99	2.5	280	94	470	520	1.10
$\mathbf{2S_{5k}}$	1.1 ± 0.1	620 ± 70	92	0.95	730	82	480	510	1.15
$\mathbf{3S_{5k}}$	0.64 ± 0.07	1100 ± 100	80	0.61	1100	69	400	500	1.32
$\mathbf{1L_{4k}}$	8.1 ± 0.7	87 ± 9	>99	6.9	99	96	530	420	1.01
$\mathbf{2L_{4k}}$	5.1 ± 0.4	140 ± 10	>99	4.5	160	95	530	460	1.01
$\mathbf{3L_{4k}}$	1.7 ± 0.3	420 ± 70	>99	1.2	560	88	390	400	1.29

[a]Polymerizations were conducted in $CHCl_3$ (or $CDCl_3$) with [MM]/[**G3**] = 100 at [MM] = 50 mg/mL at rt. [b]Calculated from conversions from ^{1}H NMR spectroscopy using first-order kinetic analysis. [c]Calculated using $t_{1/2} = \ln(2)/k_p$. [d]Measured by monitoring olefin consumption using ^{1}H NMR spectroscopy. [e]Determined using conversions measured by SEC. [f]Measured using SEC by comparing the relative integrations of the bottlebrush and MM peaks in the RI trace (95% represents full conversion for MMs $\mathbf{1-3S_{3k}}$ due to the existence of initiator-derived chains; see Figure S39). [g]Measured by SEC using absolute MW determined by light scattering. [h]Determined using the formula $M_{n,expected} = M_{n,MM} * conv * ([MM]/[\mathbf{G3}])_0$. [i]These data represent the conversion and MW achieved after 24 h.

selected anchor groups would follow the trend of propagation rate **1** > **2** > **3**.

Macromonomer Synthesis. Polystyrene MMs of number-average MW (M_n) ≈ 3 kDa were synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization using three different norbornene functionalized chain transfer agents (CTAs) containing the anchor groups shown in Figure 1A. Low AIBN loadings (0.01 equiv relative to CTA) were employed during RAFT polymerization to avoid radical reactions involving the norbornene olefins, to reduce the proportion of initiator-derived chains, and to limit the incidence of termination by coupling, which would result in polymers functionalized with norbornene groups on both chain ends.[26,39−41] Despite our efforts, ROMP of $\mathbf{1S_{3k}}$ at different [MM]/[**G3**] ratios revealed the presence of ∼5% of initiator-derived chains, as grafting-through using this MM reached a maximum conversion of 95% regardless of the targeted DP (Figure S39), with quantitative consumption of norbornene olefin. In addition, to establish whether the proposed anchor group effect is consistent across other MMs of varying repeat unit structure and MW, a series of higher MW polystyrene MMs (∼5 kDa) were synthesized by increasing the [S]/[CTA] ratio. Three poly(lactic acid) (PLA) MMs (∼4 kDa) were also prepared via DBU-catalyzed ring-opening polymerization (ROP) of D,L-lactide using three different norbornene alcohols as initiators in accordance with a previously reported procedure.[42] ^{1}H NMR spectroscopy and size exclusion chromatography (SEC) were employed to characterize the

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resulting MMs. In all cases, the MMs possessed narrow molecular weight distributions, low dispersities ($Đ$), and M_n values consistent with conversions determined by ^{1}H NMR spectroscopy (Table S1).

^{1}H NMR Kinetic Analysis. Our principal kinetic analysis of ROMP grafting-through of MMs containing anchor groups **1**, **2**, and **3** was conducted using in situ ^{1}H NMR spectroscopy by monitoring the disappearance of the resonance corresponding to the olefin protons of the terminal norbornene relative to protons from the side-chain repeat units of the MMs, which remain constant (Figure S11). Conversions determined using this method were averaged over multiple runs and utilized to calculate propagation rate constants and half-lives. ROMP mediated by catalyst **G3** can be considered as pseudo-first-order; therefore, first-order kinetic analysis was applied. As is evident in Table 1 and Figure 1B, a substantial dependence of the rate of MM consumption on the anchor group was observed, with k_p values differing by a factor of 7 across MMs **1**−**3S$_{3k}$**. The rate of propagation of the MMs followed the trend based on their anchor groups of **1** > **2** > **3**.

Kinetic analysis of polystyrene MMs of MW ≈ 5 kDa with anchor groups **1**, **2**, and **3** revealed the same trend in propagation rates. Consistent with literature reports, an overall decrease in k_p was observed upon increasing the MM size, likely resulting from increased steric congestion surrounding the propagating catalyst.[31,32,43] The terminal conversions achieved during ROMPs of these MMs were also reduced compared to the 3 kDa set. For example, **3S$_{3k}$** reached a conversion of 91% after 1 h while **3S$_{5k}$** only attained 80% conversion in the same time. The kinetics of ROMP of PLA MMs (**1**−**3L$_{4k}$**) exhibited the same dependence on the anchor group, with k_p trending as **1** > **2** > **3**. These data indicate that this trend in anchor groups is likely to be broadly conserved, regardless of MM size or the type of repeat unit.

SEC Kinetic Analysis. A similar kinetic investigation was conducted using an SEC-based method. The sampling procedure included taking aliquots of the reaction mixture and injecting them into a solution containing ethyl vinyl ether (EVE) to terminate the polymerization at each time point. Conversions were determined via SEC by comparing the relative integrations of the MM and bottlebrush polymer peaks in the refractive index (RI) traces. Similar to our ^{1}H NMR spectroscopic analysis, propagation rate constants and half-lives were calculated from these conversions employing pseudo-first-order kinetic analysis. The same trend in the relative rates of propagation observed during the in situ NMR experiments, **1** > **2** > **3**, was also clear in the SEC experiments, with half-lives differing by a factor of 4−6 for the different anchor groups across each series. ROMPs of MMs **1**−**3S$_{3k}$** in CH_2Cl_2 and THF, common solvents for Ru-catalyzed metathesis, also conformed to the aforementioned trend and gave rates similar to those measured in $CDCl_3$ (Table S2).

In addition to half-life data, the SEC kinetic studies gave information regarding the control of the polymerization through evaluation of the shape and $Đ$ of the bottlebrush polymer molecular weight distributions. M_n and $Đ$ values were compared for the bottlebrush polymers after 24 h of ROMP grafting-through polymerization. The consequences of the observed difference in rate for different anchor groups are exemplified by these data. When the rate of propagation is slow during ROMP of MMs, in this case as the result of the anchor group effect, a broadening of the molecular weight distribution and a more pronounced disagreement between measured and theoretical M_n is observed. Further, both the conversion of the polymerization and the DP obtained during ROMP of MMs decrease as a function of decreasing propagation rate. This effect is most apparent for larger MMs, as is the case with **3S$_{5k}$**. Here, the conversion obtained after 24 h decreased by 25% compared to **1S$_{5k}$**, with the only notable difference in the two MMs being the chemical structure of the anchor group. Incomplete conversion within the window of catalyst lifetime leads to undesired termination (as evidenced by the substantial tailing observed in the bottlebrush molecular weight distributions of MMs **3S$_{5k}$** and **3L$_{4k}$** in particular as well as in deviations from linearity in their first-order kinetic plots); thus, control over the polymerization is eroded. Additionally, incomplete conversion leads to bottlebrush polymer samples that are contaminated with linear MM impurities.

Origin of the Anchor Group Effect. In an effort to understand the chemical origin of the observed rate differences among anchor groups, we next explored the possibility of modifying the rate of propagation of MMs **1**−**3S$_{3k}$** through the use of additives. A number of compounds have been employed during Ru-catalyzed cross-metathesis or ROMP to improve reaction rates, increase yields, or influence product stereochemistry. For example, Lewis acids have been used to coordinate with functional groups that interfere with catalyst turnover.[44,45] In particular, titanium(IV) tetraisopropoxide (TTIP) has been shown to destabilize six- and seven-membered ring chelates that form between Ru-based metathesis catalysts and carbonyl-containing substrates.[46] We chose to evaluate the effect of TTIP on the process of bottlebrush formation to disrupt the potential chelation interactions proposed between the MMs and the Ru center. In addition to this action, TTIP can scavenge pyridine; therefore, the effect of addition of trifluoroacetic acid (TFA) in the ROMP of MMs **1**−**3S$_{3k}$** was also studied for comparison.

ROMP kinetics of MMs **1**−**3S$_{3k}$** were reevaluated in the presence of TTIP (2 or 100 equiv with respect to **G3**) or TFA (2 equiv with respect to **G3**) in $CDCl_3$. For these experiments, MMs and additives were dissolved in a solution of $CDCl_3$, and the polymerizations were initiated via addition of a solution of **G3**. Aliquots of the reaction mixtures were removed at various time points, quenched with EVE, and then analyzed by SEC. The results of this study are summarized in Table 2. In all cases, the previously observed trend in k_p of MMs **1**−**3S$_{3k}$** was maintained. Addition of TTIP to the polymerizations, regardless of the amount added, had no appreciable effect on the kinetics of the polymerizations. If chelation between the anchor group and the Ru catalyst were the cause of the observed differences in rates, addition of TTIP would have been expected to enhance the rates of propagation of MMs **2S$_{3k}$** and **3S$_{3k}$**. Interestingly, addition of 2 equiv of TFA had an

Table 2. Evaluation of Additives on ROMP of MMs 1S$_{3k}$−3S$_{3k}$[a]

	Additive k_p (10^{-3} L * mol^{-1} * s^{-1})[b]			
MM	none	TTIP (2 equiv)	TTIP (100 equiv)	TFA (2 equiv)
1S$_{3k}$	8.0	6.3	6.1	>60
2S$_{3k}$	3.6	3.7	3.2	7.9
3S$_{3k}$	1.6	1.0	0.9	5.8

[a]Polymerizations were conducted in $CDCl_3$ with [MM]/[**G3**] = 100 at [MM] = 50 mg/mL. [b]Determined from MM conversions using SEC.

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effect on the k_p of all MMs, enhancing the rate dramatically in the case of $\mathbf{1S_{3k}}$ and moderately for $\mathbf{2S_{3k}}$ and $\mathbf{3S_{3k}}$.

These results contradicted our initial hypothesis of anchor group carbonyl chelation, as TFA is unlikely to disrupt these types of interactions. Instead, it ostensibly acts as a scavenger of pyridine. Pyridine concentration affects the equilibrium between the dormant and active catalyst species and seems to play a critical role in the ROMP of MMs.[47,48]

To further investigate the chelation process, we performed density-functional theory (DFT) calculations of the resting states of the alkylidene Ru catalyst for all three anchor groups after ring-opening of a single monomer unit in the chelated and nonchelated forms (Figure S40, Table S3). The DFT calculations revealed that there is not a large driving force for chelation in any of the monomers. Even though chelated species occurring via formation of six-membered rings are possible, the calculated $\Delta G_{chelation}$ values are between zero and −5 kcal/mol. Moreover, stable chelated species were not found for one of the regioisomers of both MM $\mathbf{1S_{3k}}$ and MM $\mathbf{2S_{3k}}$, as they involve formation of larger rings. We note that the formation of a chelated species from the unchelated isomer involves a rotation around a Ru═C−C−C dihedral angle of the alkylidene, which might incur an energetic penalty. In effect, potential energy surface scans of this coordinate indicate that the chelation process is activated, involving barriers of ∼5 kcal/mol. Both the relatively low exoergicity of the chelation process and the presence of barriers for chelation obtained from the DFT calculations further dispute the chelation hypothesis.

Instead of resulting from a possible chelation process, we propose that the differences in k_p between MMs $\mathbf{1}$−$\mathbf{3P_y}$ derive from at least two considerations. First, the capability of MMs $\mathbf{1P_y}$ and $\mathbf{2P_y}$ to form regioisomers in which the anchor group is placed away from the Ru center may be the primary cause of the difference in k_p between MMs $\mathbf{1P_y}$/$\mathbf{2P_y}$ and MM $\mathbf{3P_y}$. Second, the electronic structure of the monomer likely plays a role in the overall reaction rate. A key step in the ROMP mechanism is the addition of the monomer to the alkylidene Ru catalyst. Since species with a higher-energy HOMO exhibit greater reactivity in addition reactions, monomers with anchor groups that raise the HOMO energy might result in a larger overall polymerization rate. DFT calculations of small molecule analogues of MMs $\mathbf{1}$−$\mathbf{3P_y}$ (Figure S41) indeed revealed that the HOMO stability of the monomers (MM $\mathbf{1P_y}$ < MM $\mathbf{2P_y}$ < MM $\mathbf{3P_y}$) is inversely correlated with the measured k_p values (MM $\mathbf{3P_y}$ < MM $\mathbf{2P_y}$ < MM $\mathbf{1P_y}$). The fact that monomers with higher HOMO energies result in faster polymerization rates lends support to the idea that the anchor groups can modulate the reaction rate by influencing the electronic structure of the monomer.

Consequences of Anchor Group Choice. The backbone DP and the purity of the polymer sample are critical parameters to consider when designing chemical syntheses to prepare bottlebrush polymers. Indeed, the ultimate three-dimensional shape (i.e., globular vs cylindrical) and physical properties depend on the fine-tuning of these parameters, with most applications targeting bottlebrush polymers with high DPs and purity. It is clear that anchor group chemistry affects the kinetics of ROMP of MMs. However, the >4-fold difference in k_p may not fully convey the importance of the configuration of the handful of atoms that connect the polymer chain to the norbornene.

To underscore the importance of the differences in the kinetics of reaction between MMs observed here, we targeted high backbone DPs for polymerizations using the fastest and slowest propagating anchor groups. For these experiments, ROMP of $\mathbf{1L_{4k}}$ and $\mathbf{3L_{4k}}$ was conducted at increasing [**MM**]/[**G3**] ratios (50−1000) under our optimized conditions (50 mg/mL, $CHCl_3$, 24 h), and the resulting bottlebrush polymers were analyzed by SEC (Figure 2B). As shown in Figure 2C, the

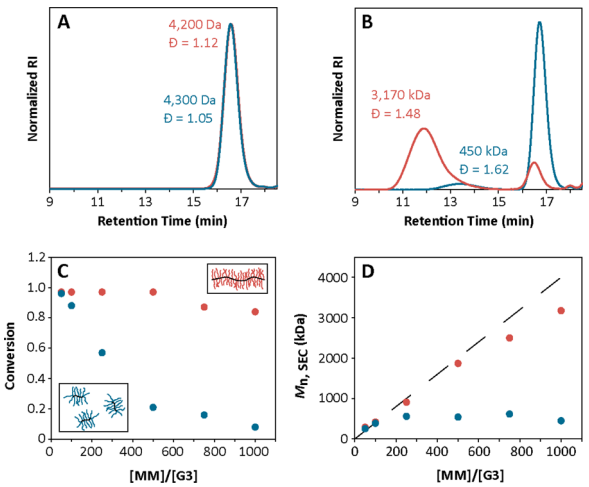

Figure 2. ROMP grafting-through with increasing [**MM**]/[**G3**] ratios for MMs $\mathbf{1L_{4k}}$ (red) and $\mathbf{3L_{4k}}$ (blue). (A) SEC traces of both MMs. (B) SEC traces (RI detector) of bottlebrush polymers resulting from ROMP of both MMs at [**MM**]/[**G3**] = 1000. (C) Conversion (as measured by SEC) vs [**MM**]/[**G3**] for both MMs. (D) M_n (as measured by SEC) as a function of [**MM**]/[**G3**] for both MMs. The dashed line represents the theoretical molecular weight based on the [**MM**]/[**G3**] ratio.

conversion of the polymerization remained relatively constant throughout the [**MM**]/[**G3**] series for MM $\mathbf{1L_{4k}}$. In stark contrast, the conversion of MM $\mathbf{3L_{4k}}$ decreased rapidly with increasing [**MM**]/[**G3**]. A plot of M_n vs [**MM**]/[**G3**] (Figure 2D) illustrates the concept of a backbone DP ceiling for a set of experimental conditions, with an ROMP of $\mathbf{3L_{4k}}$ limited to a DP of ∼100 repeat units regardless of the targeted [**MM**]/[**G3**]. However, using $\mathbf{1L_{4k}}$ it was possible to synthesize a bottlebrush polymer with an M_n in excess of 3000 kDa (Figure 2B), approximately an order of magnitude larger than the bottlebrush polymer prepared using an MM of nearly identical M_n with the same repeat unit. It should be further emphasized that this broad discrepancy in obtainable DP arises entirely from the chemical structure of the anchor group (Figure 2A shows SEC traces of MMs $\mathbf{1L_{4k}}$ and $\mathbf{3L_{4k}}$ to exemplify the similarity of the MM molecular weight distributions) and that this phenomenon primarily originates from the kinetics of polymerization.

CONCLUSIONS

Our kinetic analyses of ROMP grafting-through support our hypothesis that the anchor group has a large effect on polymerization kinetics and the ultimate MW of the bottlebrush polymer. The observed trend (k_p of anchor group **1** > **2** > **3**) was conserved for polystyrene MMs of different MWs as well as for PLA MMs. We initially proposed a chelation mechanism to explain the observed differences in propagation rate. However, experimental and computational studies showed that this phenomenon more likely originates from a combination of steric effects and differences in

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monomer electronic structure. Addition of TFA to polymerizations of MMs **1**−**3S**$_{3k}$ enhanced the rate of propagation, demonstrating the critical role of pyridine concentration in the ROMP of MMs. Importantly, the >4-fold difference in the propagation rates between the three different anchor groups had a dramatic effect when targeting high bottlebrush backbone DPs. Bottlebrush polymers with MWs > 3000 kDa could be prepared from **1L**$_{4k}$. However, using **3L**$_{4k}$, the maximum obtainable MW was nearly an order of magnitude lower (~450 kDa) and corresponded with a relatively broad molecular weight distribution and low conversion. Given that the properties of these complex macromolecules depend on factors such as the backbone DP and the purity of the polymer sample, rational selection of the anchor group is a critical factor when designing synthetic strategies for preparing bottlebrush polymers. We expect that this anchor group effect may also be important for polymerization of other challenging monomers, such as those with peptides, sugars, dendrimers, or other bulky groups.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b13317.

Synthetic and experimental details, characterization data, computational data (PDF)

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Notes

The authors declare no competing financial interest.

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