

The influence of the norbornene anchor group in Ru-mediated ring-opening metathesis polymerization:

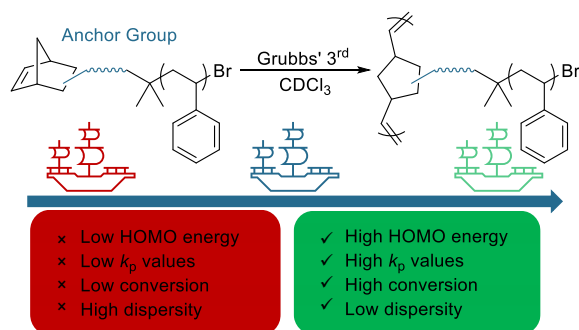
Synthesis of bottlebrush polymers

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ABSTRACT

Ring-opening metathesis polymerization (ROMP) mediated by Grubbs' third-generation catalyst [G3, (H₂IMes)(Cl)₂(pyr)₂RuCHPh] is widely used to make bottlebrush polymers by polymerization of a macromonomer (MM), typically a low molecular weight polymer

functionalized with a norbornene. Termed the grafting-through method, this strategy requires a high degree of living character (“livingness”) to form well-defined bottlebrush polymers. Here we studied how various anchor groups, the series of atoms connecting the polymerizable norbornene unit to the polymer side-chain, affect livingness in ROMP in a series of *exo*-norbornene polystyrene MMs. First, we calculated the HOMO and HOMO/LUMO gap energies of MM structures containing five different anchor groups using density functional theory methods, finding that these energies spanned a range of 10 kcal/mol. We then performed kinetics experiments on each MM with target backbone degrees of polymerization (N_{bb}) of 100 to measure the propagation rate constant ($k_{p,obs}$) under identical conditions. A positive correlation between the HOMO energy and measured $k_{p,obs}$ values emerged, revealing a 7-fold variation in $k_{p,obs}$ values across the five MMs, suggesting different degrees of livingness among the anchor groups. A series of studies targeting N_{bb} values ranging from 100 to 2000 further highlighted these differences: The MMs with high $k_{p,obs}$ values reached higher conversions at high target N_{bb} values with lower dispersities ($\mathcal{D}$) than the MMs with lower $k_{p,obs}$ values. Finally, we evaluated the synthesis of bottlebrush pentablock copolymers using the MMs at the two extremes by injecting an MM aliquot into a catalyst solution five consecutive times, allowing for polymerization of each block before the next injection. MM conversion at each step was higher, and the $\mathcal{D}$ values for each block were lower, for the MM with the highest k_p anchor group compared to the lowest k_p anchor group. Taken together, these studies highlight how the anchor group dramatically affects both k_p and livingness in ROMP, which is crucial for the synthesis of precise bottlebrush (co)polymers.

INTRODUCTION

Complex synthetic polymer architectures (topologies) have garnered interest over the years due to their ability to capture intricate properties found in nature. A particularly interesting one is bottlebrush polymers, which contain polymer backbones with densely grafted polymeric side-chains, similar to the topology of proteoglycans.¹⁻⁵ The densely packed side-chains prevent entanglement of these macromolecules, influencing properties such as elasticity and domain size in solid state materials, and nanoscopic size and shape in solution.⁵⁻¹⁰ As a result, bottlebrush polymers have many potential applications including as elastomers with unusual properties,¹¹⁻¹⁶ as carriers in biomedicine/drug delivery,¹⁷⁻¹⁹ and as photonic crystals,²⁰⁻²² and semiconductors.²³⁻²⁷ Tuning properties in these materials is achieved through adjusting the backbone and side-chain degree of polymerization (N_{bb} and N_{sc} , respectively), as well as grafting density (z , the fraction of monomer units that contain side-chains).⁶ However, control over these structural features of the resulting polymers is sometimes lost at high N_{bb} or N_{sc} , especially when z is near 1. Therefore, living polymerizations are vital for the synthesis of bottlebrush polymers as they allow for control over molecular weight, molecular weight distribution, and retention of chain end functionalities on the side-chains and backbone.²⁸⁻²⁹

Living polymerizations are chain polymerizations that lack chain termination and irreversible chain transfer, and in most cases, a fast initiation process enables them to maintain a constant number of kinetic-chain carriers throughout the polymerization.³⁰ Historically, anionic polymerization was preferred for synthesizing bottlebrush polymers,³¹⁻³³ although they were simply referred to as densely grafted polymers until the mid-1990s.³⁴ More recently, many other polymerization methods that exhibit living characteristics (i.e., “livingness”) have been used to synthesize either the backbones or side-chains of bottlebrush polymers, such as atom-transfer

radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization.³⁵⁻³⁷ Since Bowden's seminal work in 2004,¹ ring-opening metathesis polymerization (ROMP) is also commonly used due to its high propagation rates (k_p), high functional group tolerance, and relative insensitivity to air and water.³⁸ Mediated by a transition metal catalyst such as Grubbs' third-generation catalyst [G3, (H₂IMes)(Cl)₂(pyr)₂RuCHPh], ROMP typically has high propagation rates and even higher initiation rates, enabling living characteristics.³⁹ Low termination rates (k_t) are also critical in polymerizations with a high degree of living character, where livingness is defined as k_p/k_t . In the context of ROMP, termination occurs primarily through catalyst decomposition,⁴⁰ with a rate that is generally low, making it a well-suited method for the synthesis of complex architectures such as bottlebrush polymers.

In most cases, ROMP enables the synthesis of well-defined bottlebrush polymers via the polymerization of norbornene-functionalized macromonomers (MMs).⁸⁻⁹ The collective synthesis of MMs followed by ROMP is referred to as the grafting-through technique, and it enables control over N_{sc} and N_{bb} , with the capacity for perfect grafting density ($z = 1$).⁴¹ However, despite the popularity of ROMP for making complex polymer topologies, bottlebrush polymers prepared by ROMP grafting-through tend to be fairly small due to the loss of living character when polymerizing even moderately sized MMs ($N_{sc} = 50$ – 100) to moderate degrees of polymerization ($N_{bb} = 100$ – 200). This is because k_p is lower in MMs than in small molecule monomers.⁴²⁻⁴⁴ It is worth noting that this phenomenon is not limited to ROMP—Sheiko and coworkers recently described similar rate decreases between monomers and MMs in ATRP.⁴⁵ In contrast to k_p , k_t in ROMP is unlikely to be affected by the length of MM side-chains because it is a function of catalyst decomposition, which primarily (although not entirely) occurs through an intramolecular C–H activation pathway that does not depend heavily on monomer type.⁴⁶⁻⁴⁷ Therefore, while ATRP

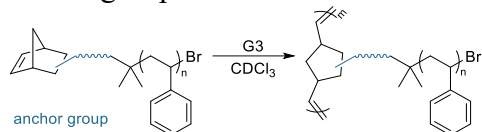
and RAFT achieve high livingness (as quantified by high k_p/k_t ratios)⁴⁸ by reducing k_t , this option is not available in ROMP using G3 catalyst. Instead, one needs to enhance k_p to increase livingness in ROMP.

In 2016 we enhanced the k_p of ROMP mediated by G3 catalyst by tuning MM reactivity.⁴⁹ In a recent paper, we presented a thorough investigation of this phenomenon through a combined computational and experimental approach, measuring propagation and termination rates of small molecule monomers in the synthesis of linear polymers.⁵⁰ In this recent work, we monitored the polymerization of eight different monomers mediated by G3 catalyst as well as the less active Grubbs 1st generation catalyst [G1, (PCy₃)₂(Cl)₂RuCHPh]. The monomers had varying anchor groups, which is the series of atoms directly connected to the polymerizable unit used in ROMP (norbornene here).⁵¹ We found that the anchor group influenced the energy of the HOMO localized on the norbornene olefin and that an increasing HOMO energy increased k_p but did not substantially affect k_t . However, when using the highly active G3 catalyst, the effect on k_p reached a plateau for the three monomers with the highest HOMO energies, where k_p remained flat despite a continued increase in the HOMO energy. Interestingly, when using G1 catalyst, where k_p values were 10–20-fold lower than in G3 catalyst, we saw larger variations in k_p for the three monomers that plateaued in rate with G3 catalyst. Therefore, we hypothesized that adding a side-chain (i.e., using an MM instead of a small molecule norbornene) would slow down polymerization enough for the HOMO energy to influence k_p in MMs with these three anchor groups. In other words, we envisioned that adding a side-chain would allow us to observe differences among these “fast” (i.e., high k_p) anchor groups that were unobservable in small molecule norbornenes.

Here we focus on the ROMP of MMs, quantitatively investigating how the anchor group affects k_p and livingness in the synthesis of bottlebrush polymers (Scheme 1). We set out to study

five anchor groups of interest, specifically those suitable for attaching a polymer chain to the norbornene as well as easily comparable to equivalent structures in our recent paper.⁵⁰ Through the use of computational methods to determine HOMO energy values and experimental methods to measure k_p values, we investigated the effects of the anchor group in ROMP of MMs. Additionally, we aimed to study how k_p affects livingness in ROMP by monitoring MM conversion and maximum obtainable bottlebrush polymer N_{bb} at high [MM]/[G3] ratios (up to 2000). We also anticipated that livingness could be assessed by synthesizing bottlebrush pentablock copolymers in a sequential addition of MMs approach by following molecular weight evolution and increases in dispersity ($\mathcal{D}$) upon the addition of each new block. Overall, we envisioned that these studies could reveal how the anchor group can be tuned to yield maximum (macro)monomer conversion and livingness when synthesizing complex polymer topologies by ROMP.

Scheme 1. Representative scheme of grafting-through ROMP of norbornene MMs with various anchor groups where $n = N_{sc}$ and $m = N_{bb}$



RESULTS AND DISCUSSION

In the recent paper mentioned in the introduction, we calculated the HOMO and HOMO/LUMO gap energies of 61 monomers with different anchor groups for the synthesis of linear polymers via ROMP.⁵⁰ All HOMOs were centered on the norbornene alkene, which interacts with the Ru center in the rate-determining metallacyclobutane formation step in ROMP.⁵² Of these 61 monomers, we selected eight anchor groups to synthesize and study experimentally with the goal of identifying the effects of the anchor group on k_p and livingness in ROMP. Here we focus

on five of these eight anchor groups, including the three that showed the highest k_p in the ROMP of small molecule norbornenes, in the form of MMs to investigate the effects of the anchor group on livingness in bottlebrush polymer synthesis.

HOMO Energy Calculations

We first calculated the HOMO energies of the five selected anchor groups attached to a polystyrene (PS) side-chain (MMs **1–5**) (Figure 1A). In these computational studies, only one styrene repeat unit, representing the PS side-chain, was used to calculate the molecular orbital energies because we aimed to investigate the HOMO localized on the reactive olefin, which should not be influenced by the side-chain beyond the first repeat unit. The HOMO energies were calculated from optimized geometries of the five monomer structures using density functional theory (DFT) (M06-2X method and def2-TZVP basis set).⁵³⁻⁵⁴ Coordinates of the five monomer structures and the HOMO energies are shown in the Supporting Information. Our goal was to investigate the π bonding orbital of the olefin, as these electrons are involved in the rate-determining step of norbornenyl ROMP, which corresponds formation of the metallocyclobutane intermediate from the olefin and metal carbene.⁵² In MMs *x*-MOM₂E'-PS (**1**) and *x*-ME'-PS (**2**), the π bonding orbital was the absolute HOMO (HOMO-0), but in some monomers, this orbital did not correspond to the absolute HOMO. For the anchor group in MM *x*-EM₂E'-PS (**3**), the olefin-centered HOMO was HOMO-1, for MMs *xx*-IMEM₂E'-PS (**4**) and *xx*-IM₂E'-PS (**5**), it was HOMO-2. For the sake of simplicity, we use the term HOMO to refer to "olefin-centered HOMO" in the rest of this paper.

The HOMOs localized on the reactive olefins span energies in the -197 to -187 kcal/mol range, similar to analogous small molecule structures in our related paper.⁵⁰ In this related paper,⁵⁰

we also calculated the HOMO/LUMO energy gap for each monomer based on the concept that multiple orbital interactions occur during the formation of the metallocyclobutane ring, as suggested by Suresh and Koha.⁵⁵ Here, we hypothesized that MMs with higher norbornene HOMO energies and lower LUMO olefin energies would exhibit faster polymerization rates (k_p values) and higher livingness in general, as measured in maximum obtainable N_{bb} studies and bottlebrush pentablock copolymer chain extension studies.

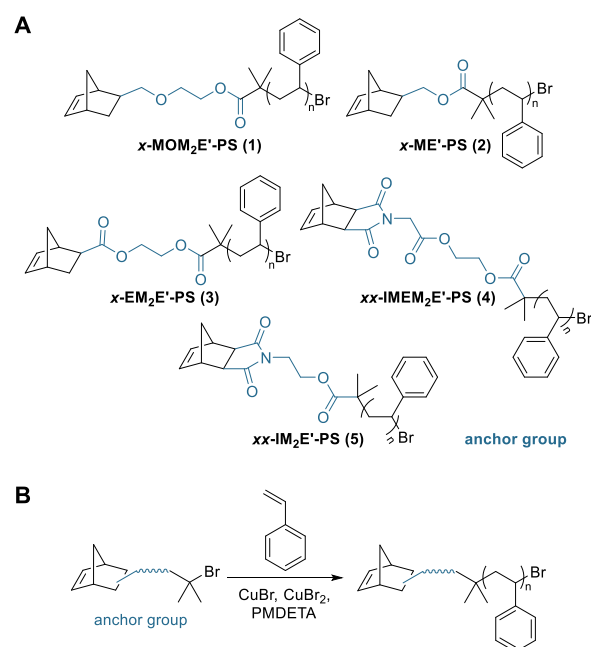


Figure 1. (A) Norbornene MMs with various anchor groups (blue) computationally and experimentally investigated where $n = N_{sc}$. For computations, $N_{sc} = 1$ and the Br end group was replaced with H; for experiments, $N_{sc} = 24\text{--}28$. All monomers exhibited *exo* (x prefix) or *exo-exo* (xx prefix) stereochemistry. Letters identify structural components of the anchor group from left to right (M = methylene, O = oxygen, E = ester with carbonyl on the left, E' = ester with carbonyl on the right, I = imide); all MM side-chains are polystyrene (PS). Subscripts indicate the number of times that component is repeated. (B) Representative synthesis of PS MMs via ATRP. Polymerizations were conducted at 90 °C for 3 h targeting 10% conversion of styrene.

We employed ATRP to synthesize five PS MMs (Figure 1B), all with number-average molecular weight values (M_n) near 3 kg/mol. We designed these MMs to have the same polymer side-chain and M_n to isolate the contributions of the anchor group on k_p . Each was synthesized using the direct-growth approach from five different norbornene-derived initiators (Table 1). Standard conditions of Cu(I)Br, Cu(II)Br, and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) were used in all cases and polymerizations were conducted at 90 °C for 3 h. We targeted 10% monomer conversion in the ATRP reactions to avoid termination by coupling, which would result in MMs with norbornene groups on both chain ends.⁵⁶

Because any residual impurities, in particular styrene monomer but also Cu catalyst or ligand, could detrimentally affect the rate of ROMP,⁵⁷⁻⁵⁹ we extensively purified each MM. In brief, crude MMs were diluted with water and extracted with ethyl acetate to remove Cu species, then purified by automated silica gel chromatography using an ethyl acetate/hexane gradient as the mobile phase. After solvent removal, each MM was passed through basic alumina in tetrahydrofuran (THF), and finally precipitated into methanol. Automated flash chromatography, which monitors UV absorbance throughout the separation (Figures S15–S19), provided confidence in the removal of all residual monomer through the clear separation between the styrene peak that elutes first and the broad MM peak that elutes later, as we showed previously.⁵⁶ Passage of the polymer solution through an alumina plug after column purification presumably removed trace catalyst and/or ligand that remained; we observed lower conversion to bottlebrush polymer when this step was not carried out. A final precipitation step into methanol afforded the final MM products as white powders, making them easy to work with for the subsequent ROMP step.

Table 1. Characterization of PS MMs

MM	$M_{n,SEC}^a$	$M_{n,NMR}^b$	$\bar{D}^a$
	(kg/mol)	(kg/mol)	
<i>x</i> -MOM ₂ E'-PS (1)	3.2	2.9	1.06
<i>x</i> -ME'-PS (2)	3.2	3.3	1.08
<i>x</i> -EM ₂ E'-PS (3)	2.9	3.2	1.07
<i>xx</i> -IMEM ₂ E'-PS (4)	2.9	3.3	1.09
<i>xx</i> -IM ₂ E'-PS (5)	2.9	3.4	1.06

^aMeasured by SEC in THF at 30 °C with multiangle light scattering. ^bMeasured by end-group analysis via ¹H NMR spectroscopy. See Figures S20–S29.

Each MM was next polymerized via ROMP to investigate the differences in $k_{p,obs}$ based on the anchor group. Polymerizations of all MMs were mediated by G3 catalyst with a targeted N_{bb} of 100 at a concentration of 20 mM in CDCl₃, under air and at room temperature. Aliquots were removed and terminated with an excess of ethyl vinyl ether at predetermined time intervals, the solvent was removed, and each aliquot was then analyzed by size exclusion chromatography (SEC). MM conversion at each time point was measured by comparing the areas of the MM peak and bottlebrush polymer peak. Average $k_{p,obs}$ values and half-lives were calculated from first-order kinetics plots for at least three polymerizations per MM. The conversion versus time data and first-order fits are shown in Figure 2 for a representative MM, *x*-MOM₂E'-PS (1). Similar graphs for the other four MMs are included in the Supporting Information (Figures S30–S39).

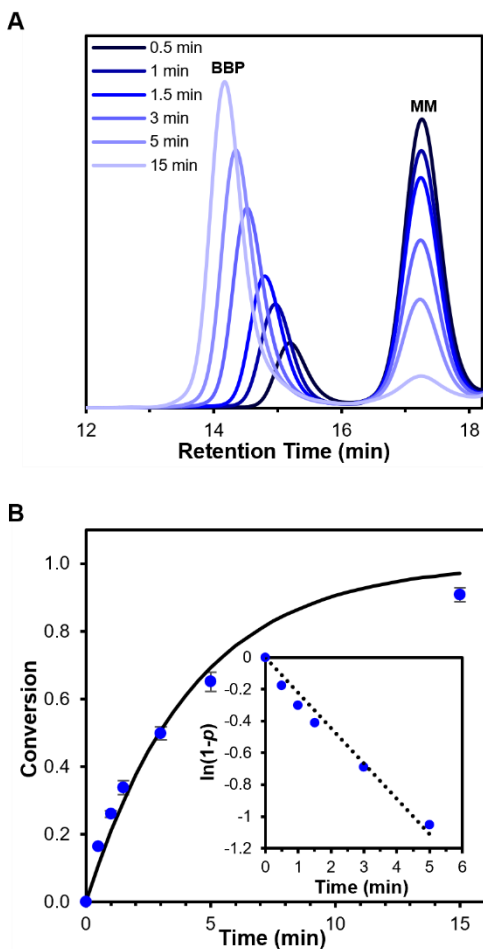


Figure 2. (A) Representative SEC traces (dRI signal) of the ROMP of MM *x*-MOM₂E'-PS (**1**) at an [MM]/[G3] ratio of 100:1. As the polymerization proceeds, the MM signal at 17.2 min decreases in intensity and the bottlebrush polymer signal increases in intensity and shifts in retention time from 15.2 min to 14 min. (B) Kinetic analysis of the ROMP of MM *x*-MOM₂E'-PS (**1**) in CDCl₃ at an [MM]/[G3] ratio of 100:1 and [MM] = 20 mM. The solid line represents the fit to the averaged conversion data based on the equation $p = 1 - e^{(-k_{obs}t)}$ where p = fractional conversion.

As expected, each MM polymerized slower, by approximately an order of magnitude, compared with analogue small molecule monomer structures,⁵⁰ where the only difference lies in the presence of the PS side-chain. MM *x*-ME'-PS (**2**) had the highest $k_{p,obs}$ out of all the MMs tested and polymerized 7-fold faster than the MM with the lowest $k_{p,obs}$ [*xx*-IM₂E'-PS (**5**)]. MMs **1–3** all had half-lives under 4 min, whereas the imide-based MMs (**4–5**) had half-lives over 13 min. Relatively low dispersities and good agreement between expected and measured M_n values

for the resulting bottlebrush polymers suggest high livingness in all of these polymerizations (Table 2).

Table 2. HOMO energies, HOMO/LUMO gap energies, polymerization kinetics, and bottlebrush polymer characterization for ROMP of MMs **1–5**

MM	HOMO Energy ^a (kcal/mol)	HOMO/ LUMO Gap (kcal/mol) ^a	$k_{p,obs}^b$ (min ⁻¹)	$t_{1/2}$ (min)	% conv ^c	BB $M_{n,expected}^d$ (kg/mol)	BB $M_{n,SEC}^e$ (kg/mol)	BB $\bar{D}^e$
<i>x</i> -MOM ₂ E'-PS (1)	-187	214	0.23 ± 0.02	3.0 ± 0.2	98	320	325	1.06
<i>x</i> -ME'-PS (2)	-187	214	0.31 ± 0.03	2.3 ± 0.2	98	320	295	1.04
<i>x</i> -EM ₂ E'-PS (3)	-191	211	0.19 ± 0.01	3.7 ± 0.1	98	290	296	1.05
<i>xx</i> -IMEM ₂ E'-PS (4)	-196	217	0.052 ± 0.01	13.4 ± 0.3	98	290	251	1.07
<i>xx</i> -IM ₂ E'-PS (5)	-197	218	0.040 ± 0.003	17 ± 1	98	290	302	1.07

^aCalculated using M06-2X method and def2-TZVP basis set.⁵³⁻⁵⁴ ^bCalculated from conversions measured by SEC on aliquots removed at specific time points during the polymerizations. A minimum of three polymerizations were run for each MM. ^cMeasured on the final sample of the kinetics runs using SEC by comparing the areas of the bottlebrush polymer and MM peaks in the dRI trace. ^dDetermined using the equation $M_{n,expected} = M_{n,MM} * ([MM]/[G3])_0$. ^eMeasured on the final sample of the kinetics runs by SEC in THF at 30 °C with multiangle light scattering using the known dn/dc for PS of 0.185 mL/g.

We next examined how HOMO energy influenced k_p . By plotting the HOMO energies calculated for the MMs versus the experimentally measured $k_{p,obs}$ values, we found a positive correlation between HOMO energy and $k_{p,obs}$ for these five MMs (Figure 3). We found an inverse correlation for the HOMO/LUMO energy gaps and the $k_{p,obs}$ values for each MM (Figure S40). Evidently, multiple orbital interactions are important during the rate-determining step, but we focus here on the HOMO energy as a simple predictor for relative k_p values. Both trends were similar to the eight different anchor groups in analogous molecule monomers,⁵⁰ with MMs *x*-MOM₂E'-PS (**1**), *x*-ME'-PS (**2**), and *x*-EM₂E'-PS (**3**) with the highest HOMO energies exhibiting the highest $k_{p,obs}$ values and the MMs *xx*-IMEM₂E'-PS (**4**) and *xx*-IM₂E'-PS (**5**) with

lower HOMO energies undergoing slower polymerization. In the small molecule norbornene monomers, there were no measurable differences in $k_{p,obs}$ among monomers polymerized using G3 catalyst with anchor groups similar to those in MMs 1–3.⁵⁰ In this MM study, however, $k_{p,obs}$ values were different among these three anchor groups. Interestingly, MM *x*-ME'-PS (2) showed the highest $k_{p,obs}$ value even though MM *x*-MOM₂E'-PS (1) had a slightly higher HOMO energy, although the 0.8 kcal/mol difference between these two MMs is likely within the accuracy of the methods used.

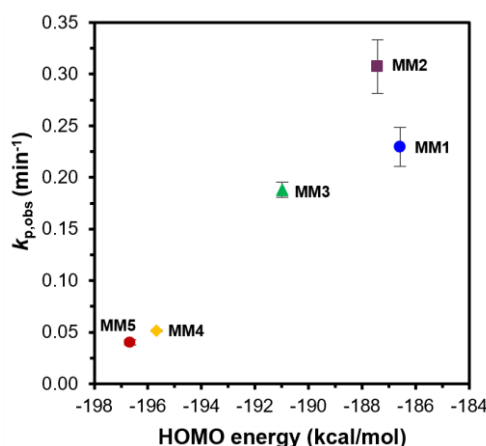


Figure 3. Measured $k_{p,obs}$ values versus HOMO energy for MMs 1–5.

Effects of the Anchor Group on Livingness in High Target N_{bb} Bottlebrush Polymers

Polymerizations that exhibit living characteristics have high k_p/k_t ratios, enabling the synthesis of polymers with high degrees of polymerization while maintaining low $\bar{D}$ values.⁴⁸ High livingness in ROMP grafting-through of MMs is critical for the synthesis of precise bottlebrush polymers. Control over M_n and $\bar{D}$ of the resulting bottlebrush polymers can be lost when targeting high N_{bb} values due to the increased number of required successful catalyst turnovers compared to polymerizations targeting low N_{bb} values. Therefore, as a method of evaluating livingness, we

designed a series of experiments examining grafting-through ROMP with high [MM]/[G3] ratios (i.e., target N_{bb} values ranging from 100 to 2000). By comparing the experimentally observed N_{bb} values (as estimated by the equation $N_{bb} = M_{n,bottlebrush}/M_{n,MM}$) to their target N_{bb} values across the five MMs studied here, we envisioned that this set of experiments would reveal the most living anchor groups, i.e., those with the highest k_p/k_t ratios. We hypothesized that MM *xx*-ME'-PS (**2**), which had the highest k_p , would exhibit the highest livingness in these experiments because anchor group choice did not substantially affect k_t in small molecule norbornenes.⁵⁰

The high target N_{bb} experiments were prepared at an MM concentration of 20 mM in CDCl₃, under air and at room temperature, similar to the kinetics experiments described above. We set the target N_{bb} (i.e., [MM]/[G3] ratio) to 100, 250, 500, 750, 1000, 1500, and 2000 for each of the MMs. Each ROMP reaction was terminated after 24 h with an excess of ethyl vinyl ether to ensure maximum conversion was reached. The solvent was removed and the residual polymer was redissolved in THF for SEC analysis. All polymerizations were run at least three times.

MM conversion versus target N_{bb} (Figure 4A) and measured N_{bb} versus target N_{bb} (Figure 4B) were plotted for all five MMs (error bars were not included in the graphs for the sake of clarity and are provided in Tables S1–S5). All MMs reached high conversion (>90%) and showed measured N_{bb} values matching target values when with an [MM]/[G3] ratio of 100:1, similar to the kinetics experiments. However, even at a modest [MM]/[G3] ratio of 250:1, MMs *xx*-IMEM₂E'-PS (**4**) and *xx*-IM₂E'-PS (**5**) failed to exceed 90% conversion and did not reach target N_{bb} values. These two MMs showed even lower conversion (<60%) and significant deviation from targeted N_{bb} with $D \sim 1.4$ at an [MM]/[G3] ratio of 500:1. Less than 3% MM conversion was observed for MM *xx*-IM₂E'-PS (**5**) at target $N_{bb} = 1000$ and higher, and MM *xx*-IMEM₂E'-PS (**4**) barely polymerized to form bottlebrush polymer at or above target $N_{bb} = 1500$. Thus, these two imide-

based anchor groups only exhibited a high degree of livingness up to $N_{bb} = 100$, consistent with the lower livingness for imide-based anchor groups in small molecule norbornenes.⁵⁰

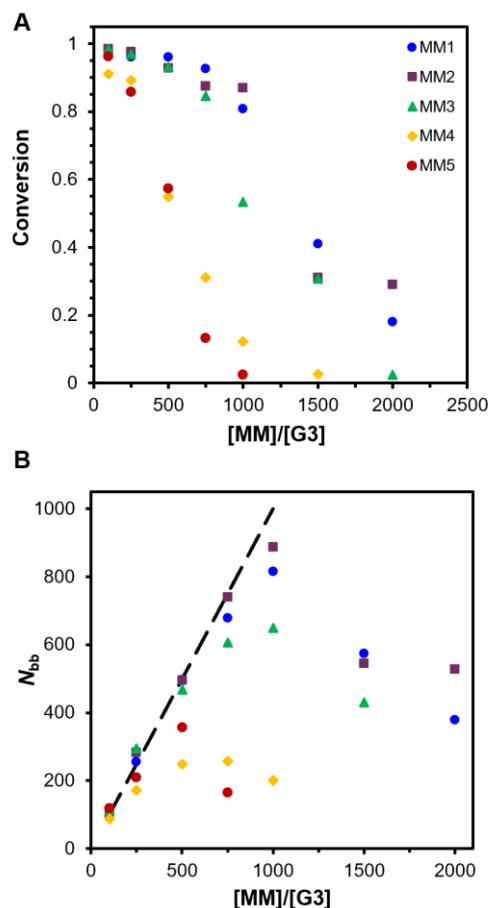


Figure 4. (A) Fractional MM conversion to bottlebrush polymer after 24 h versus target N_{bb} values, referred to as $[MM]/[G3]$ ratio, for grafting-through ROMP of the five MMs studied here. Reactions were conducted at 20 mM in MM in $CDCl_3$ under air at rt. Conversion was measured using SEC by comparing the areas of the bottlebrush polymer and MM peaks in the dRI trace. (B) Measured N_{bb} versus target N_{bb} values, referred to as $[MM]/[G3]$ ratio. The black dashed line refers to expected N_{bb} as $[MM]/[G3]$ increases. Measured N_{bb} values were determined from $M_{n,bottlebrush}$ obtained by SEC in THF at 30 °C with multiangle light scattering, calculated based on the equation $N_{bb} = M_{n,bottlebrush}/M_{n,MM}$. In both graphs, error bars were removed for better visualization of the data but can be found in Tables S1–S5.

The three MMs with higher k_p values (1–3) showed high livingness out to higher target N_{bb} values than MMs xx -IMEM₂E'-PS (4) and xx -IM₂E'-PS (5). MM x -EM₂E'-PS (3) showed >90% conversion and N_{bb} matching expected values out to a target $N_{bb} = 500$, but experienced lower

conversion and large deviations from target N_{bb} values at 750 and higher, with <3% conversion to bottlebrush polymer observed at $N_{bb} = 2000$. MMs x -MOM₂E'-PS (**1**) and x -ME'-PS (**2**), those with the highest $k_{p,obs}$ and HOMO energies, maintained high conversion (>90%) up to an [MM]/[G3] ratio of 500:1 with $\bar{D}$ values <1.2. They both reached very good conversion (>80%) with N_{bb} matching expected values out to a target $N_{bb} = 1000$, although $\bar{D}$ values increased to 1.5–1.6. A substantial drop in conversion when targeting $N_{bb} = 1500$ and higher was observed for both MMs, but some conversion was still observed even at target $N_{bb} = 2000$. Therefore, MMs x -MOM₂E'-PS (**1**) and x -ME'-PS (**2**) maintained the most livingness of all five MMs during the grafting-through ROMP process with the highest MM conversion, best control over M_n (i.e., experimentally observed N_{bb}), and lowest $\bar{D}$ values out all the MMs investigated.

It is worth noting that MM x -ME'-PS (**2**) had the highest conversion and highest observed N_{bb} when targeting $N_{bb} = 2000$ out of MMs **1–5**, even though it was not highly living at this high target N_{bb} . These results, combined with the $k_{p,obs}$ results (Table 2), suggest that the anchor group in MM x -ME'-PS (**2**) was the most living anchor group studied here. In contrast, MM xx -IM₂E'-PS (**5**) had the lowest $k_{p,obs}$ and performed the worst in the high target N_{bb} studies, making MM xx -IM₂E'-PS (**5**) the least living anchor group out of the five MMs tested. Therefore, we decided to further compare the livingness of these two MMs in chain extension studies using the sequential addition of macromonomers ROMP (SAM-ROMP) process.

Effects of the Anchor Group on Livingness in Bottlebrush Pentablock Copolymer Synthesis

Multiblock bottlebrush copolymers with three or more blocks have been recently used to make electronic materials,⁶⁰ injectable hydrogels,^{61–62} solid electrolytes,⁶³ and nanostructures with unusual shapes.^{64–65} High livingness in block copolymer synthesis is critical for complete chain

extension, so in order to evaluate the effect of the anchor group on chain extension, we conducted a series of studies on the synthesis of bottlebrush pseudo-pentablock copolymers. In these SAM-ROMP studies, we aimed to follow evolution of molecular weight and $\bar{D}$ over the course of five consecutive additions of the same MM with a target $N_{bb} = 20$ for each addition. This strategy of consecutive additions of the same MM allowed us to remove any potential variable reactivity of different MMs, but we expect that the results would be useful in making complex structures with up to five different MMs.

The first step was to determine the time required for each MM to reach near-complete conversion (>95%) at a target $N_{bb} = 20$; therefore, we conducted kinetics experiments for MM *x*-ME'-PS (**2**) and *xx*-IM₂E'-PS (**5**) with an [MM]/[G3] ratio of 20:1. Polymerizations were carried out and monitored under the same conditions and using the same methods as the other polymerizations described here. In these experiments, MM *x*-ME'-PS (**2**) had a propagation half-life of 1.4 min and MM *xx*-IM₂E'-PS (**5**) had a propagation half-life of 13.4 min, with both MMs reaching near-complete conversion based on SEC analysis at very close to 7 half-lives [10 min for MM *x*-ME'-PS (**2**) and 90 min for MM *xx*-IM₂E'-PS (**5**)].

We then set out to compare bottlebrush pentablock copolymer synthesis for the two MMs. The pentablock polymerizations via the SAM-ROMP method were conducted under the same conditions as described above, injecting 20 equiv of the same MM five times at intervals of either 10 min [MM *x*-ME'-PS (**2**)] or 90 min [MM *xx*-IM₂E'-PS (**5**)] (Figure 5A and 5E). Aliquots were removed right before each MM injection to determine conversion, M_n , and $\bar{D}$ of each block (Table 3).

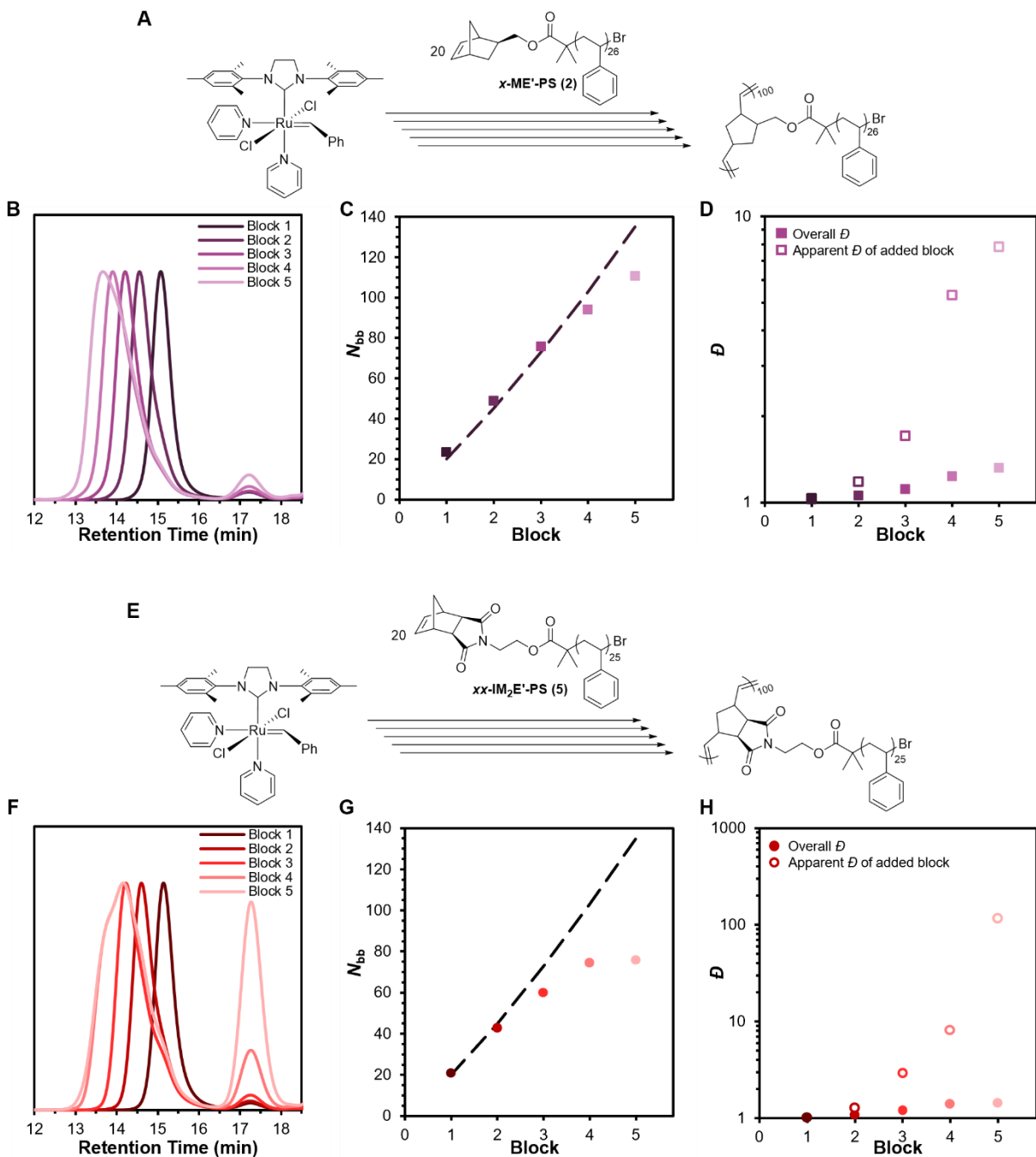


Figure 5. A and E): Schemes for bottlebrush pentablock copolymer syntheses for the ROMP of MMs x -ME'-PS (**2**) (A) and xx -IM₂E'-PS (**5**) (E). Reactions were run at a total MM concentration of 20 mM in CDCl₃ under air at rt. B and F): SEC traces (dRI signal) for the ROMP of MM x -ME'-PS (**2**) (B) and xx -IM₂E'-PS (**5**) (F) showing a decrease in retention time after each block addition. C and G): Measured N_{bb} value versus block number for the ROMP of MM x -ME'-PS (**2**) (C) and xx -IM₂E'-PS (**5**) (G). Measured N_{bb} values were determined from $M_{n,bottlebrush}$ measured by SEC in THF at 30 °C with multiangle light scattering, estimated based on the equation $N_{bb} = M_{n,bottlebrush}/M_{n,MM}$. The dashed line refers to expected N_{bb} as block number increases. D and H): Overall $\bar{D}$ and apparent $\bar{D}$ of each added block for the ROMP of MM x -ME'-PS (**2**) (D) and

xx-IM₂E'-PS (**5**) (H). Apparent $\bar{D}$ refers to the estimated dispersity of each specific block as calculated by the method developed by Harrison using the formula $\bar{D}_2 = 1 + \frac{\mu_{1+2}^2(\bar{D}_{1+2} - 1) - \mu_1^2(\bar{D}_1 - 1)}{(\mu_{1+2} - \mu_1)^2}$ where $\bar{D}_2$ is the apparent dispersity in terms of the number-average molar masses of the initial (μ_1) and final (μ_{1+2}) polymers and the overall dispersity of the initial ($\bar{D}_1$) and final ($\bar{D}_{1+2}$) polymers.⁶⁶

Table 3. Characterization of Bottlebrush Pentablock Copolymers Prepared by SAM-ROMP

MM	Block	%	BB $M_{n,expected}^b$	BB $M_{n,SEC}^c$	Total	Total	BB	Apparent
	#	conv ^a	(kg/mol)	(kg/mol)	Target N_{bb}	$N_{bb, SEC}^d$	$\bar{D}^e$	$\bar{D}^e$
<i>x</i> -ME'-PS (2)	1	97	64	70	20	23	1.03	1.03
	2	97	128	147	40	48	1.06	1.18
	3	97	192	227	60	76	1.11	1.71
	4	96	256	282	80	94	1.23	5.3
	5	95	320	332	100	110	1.32	7.8
<i>xx</i> -IM ₂ E'-PS (5)	1	97	58	60	20	21	1.02	1.02
	2	97	116	124	40	43	1.08	1.27
	3	96	174	174	60	60	1.20	2.9
	4	89	232	216	80	74	1.40	8.1
	5	71	290	220	100	75	1.43	116

^aMeasured using SEC by comparing the areas of the bottlebrush polymer and MM peaks in the dRI trace. ^bDetermined using the equation $M_{n,expected} = M_{n,MM} * ([MM]/[G3])_0$. ^cMeasured by SEC in THF at 30 °C with multiangle light scattering using the known dn/dc for PS of 0.185 mL/g. ^dDetermined using the equation $N_{bb,expected} = M_{n,bottlebrush}/M_{n,MM}$. ^eDetermined using the method developed by Harrison.⁶⁶

For both MM *x*-ME'-PS (**2**) and MM *xx*-IM₂E'-PS (**5**), we saw a decrease in the retention time of the main SEC peak upon polymerization of each additional block, indicating an increase in molecular weight of the bottlebrush polymer (Figures 5B and 5F). As expected, the first block for both MMs reached near-complete conversion (>97%) while maintaining low $\bar{D}$. However, MM conversion generally decreased after each block addition, with MM *x*-ME'-PS (**2**) dropping to 95% conversion and MM *xx*-IM₂E'-PS (**5**) dropping to just 71% conversion after the addition of all five

blocks. A small residual MM peak at 17.2 min was observed in the final SEC trace for the ROMP of MM *x*-ME'-PS (**2**), while a much more prominent MM peak remained for MM *xx*-IM₂E'-PS (**5**).

We also observed an increase in N_{bb} after each block addition, as determined by SEC, for both MMs, as expected (Figure 5C and 5G). After each injection of MM *x*-ME'-PS (**2**), a linear increase in N_{bb} was observed. All N_{bb} values generally matched target values for this MM as well, with a final estimated $N_{bb} = 110$ for the bottlebrush pentablock copolymer, close to the target N_{bb} value of 100. The small deviations from the expected values are likely due to small errors in injected monomer amount or catalyst loading. In contrast, this close agreement between target N_{bb} and measured N_{bb} values was not the case for the bottlebrush polymer derived from MM *xx*-IM₂E'-PS (**5**). A linear increase in N_{bb} matching target values was found for the first three MM injections, but blocks 4 and 5 did not reach target N_{bb} values. For this imide-based anchor group, we observed a maximum $N_{bb} = 75$, where only very little polymerization was observed for the fifth MM injection.

Comparing the bottlebrush polymer $\bar{D}$ values and the shapes of the SEC curves after every block addition for both MMs also revealed valuable insights regarding livingness. For the bottlebrush polymer derived from MM *x*-ME'-PS (**2**), $\bar{D}$ values reached 1.3, but they increased to 1.4 for the bottlebrush polymer derived from MM *xx*-IM₂E'-PS (**5**) (Table 3). Furthermore, the bottlebrush polymers with a final target $N_{bb} = 100$ for both MMs made by the SAM-ROMP method exhibited higher $\bar{D}$ values than those synthesized directly to a target N_{bb} value of 100 (1.04 for MM *x*-ME'-PS (**2**) and 1.07 for MM *xx*-IM₂E'-PS (**5**), from the kinetics data in Table 2). Additionally, low molecular weight shoulders were present in the SEC traces for blocks 4 and 5 for the ROMP of MM *x*-ME'-PS (**2**) and blocks 3 through 5 for the ROMP of MM *xx*-IM₂E'-PS

(5), suggesting some amount of chain termination in both ROMP experiments before all five blocks had been added. However, the shoulders in the SEC traces of the bottlebrush polymers derived from MM *xx*-IM₂E'-PS (5) were drastically larger than in those derived from MM *x*-ME'-PS (2), clearly indicating a lower degree of livingness for MM *xx*-IM₂E'-PS (5) compared with MM *x*-ME'-PS (2). This reduced livingness for MM *xx*-IM₂E'-PS (5) was not as readily apparent in the high target N_{bb} studies, where this MM reached a total N_{bb} of 100, matching the target N_{bb} value, with high conversion and low $\bar{D}$; however, these SAM-ROMP studies make clear that the relatively low $k_{p,obs}$ for MM *xx*-IM₂E'-PS (5) leads to low livingness when challenging the catalyst with multiple MM injections.

Only a small difference in $\bar{D}$ values (1.3 versus 1.4) between the final polymers in these two SAM-ROMP experiments was found, but we were interested in estimating the $\bar{D}$ values of each individual bottlebrush polymer block in these pentablock copolymers. Harrisson recently reported a mathematical method of estimating the apparent $\bar{D}$ of each individual block in a linear multiblock copolymer synthesis.⁶⁶ His results in a study of a 24-block copolymer made by RAFT⁶⁷ suggested that the individual substructures of complex macromolecules may be highly disperse even though the overall $\bar{D}$ remains relatively low. Using this method, we estimated the apparent $\bar{D}$ of each individual block in both bottlebrush pentablock copolymer syntheses (Figure 5D and 5H). For both MMs, the apparent $\bar{D}$ of each block increased roughly exponentially, consistent with Harrisson's analysis, but with very different outcomes between the two SAM-ROMP experiments: The final block of MM *x*-ME'-PS (2) reached an apparent $\bar{D}$ of 7.8, whereas the final block of MM *xx*-IM₂E'-PS (5) had an apparent $\bar{D}$ of 116. This order of magnitude difference between the two anchor groups dramatically demonstrates the higher degree of livingness for MM *x*-ME'-PS (2) compared with MM *xx*-IM₂E'-PS (5). The data also suggest that even with MM *x*-ME'-PS (2), the

most living anchor group studied here, there is still significant chain termination when making bottlebrush pentablock copolymers. Overall, we conclude that high k_p is critical in the ROMP of MMs to control molecular weight, maintain low dispersity, and retain high chain end fidelity when synthesizing multiblock bottlebrush copolymers, but that even for the best anchor group studied here, structural heterogeneities arise.

CONCLUSIONS

We investigated the relationship between HOMO energies localized on the norbornene olefin and livingness in the ROMP of a series of five MMs with PS side-chains of similar molecular weights but different anchor groups. DFT calculations showed that the choice of anchor group affects the norbornene HOMO energy of these MMs, and experimental results suggested that a higher HOMO energy increases the reactivity of the norbornene and increases k_p in grafting-through ROMP. Further investigation into the livingness of grafting-through ROMP through high target N_{bb} studies demonstrated that high k_p values are critical to synthesize macromolecules with precise molecular weights and low $\bar{D}$ values. MMs with lower HOMO energies (those with imide-containing anchor groups), and lower $k_{p,obs}$ values in our ROMP experiments, showed lower livingness at target $N_{bb} = 250$ and above than the other MMs. However, the two MMs with the highest HOMO energies and $k_{p,obs}$ values reached high conversion and maintained control over molecular weight when targeting N_{bb} values up to 1000. Therefore, MMs with anchor groups that lead to higher k_p values increase livingness in grafting-through ROMP compared with MMs with lower k_p values, allowing for better-defined bottlebrush polymer structures. The effect of the anchor group on livingness was further evidenced in SAM-ROMP experiments synthesizing bottlebrush pentablock copolymers using the MMs with the highest and lowest $k_{p,obs}$ values (MMs

x-ME'-PS (**2**) and *xx*-IM₂E'-PS (**5**), respectively). Each block addition of MM *xx*-IM₂E'-PS (**5**) exhibited an increase in the $\bar{D}$ value of both the overall polymer structure and the apparent $\bar{D}$ of each additional block, where the final block had a staggering apparent $\bar{D}$ of 116. A similar effect was seen for the SAM-ROMP of MM *x*-ME'-PS (**2**) to make a bottlebrush pentablock copolymer; however, the increase in apparent $\bar{D}$ was significantly lower, only reaching 7.8 for the final block.

In sum, these experiments indicate that high k_p values in ROMP are critical to maintain high livingness for the synthesis of complex macromolecules such as bottlebrush polymers, and that anchor group selection has a substantial effect on k_p . Our studies were designed to evaluate the effect of the anchor group on k_p in a defined set of MMs of similar molecular weights, but we expect that these results will suggest straightforward methods to enhance livingness and control in a wide variety of polymer topologies made by ROMP. These experiments also underscore the need to develop better anchor groups that increase k_p and better catalysts that decrease k_t in ROMP, as well as improved methods that increase the k_p/k_t ratio, to continue to expand the synthetic boundaries of complex polymer architectures.

ASSOCIATED CONTENT

Supporting Information

Supporting Information: Synthesis, NMR spectra, kinetics graphs, SEC traces, HOMO energies, and coordinates (PDF)

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Notes

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