ACS Macro Letters

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Ancillary Ligand Lability Improves Control in Cyclic Ruthenium Benzylidene Initiated Ring-Expansion Metathesis Polymerizations

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Cite This: *ACS Macro Lett.* 2023, 12, 1286−1292 Read Online

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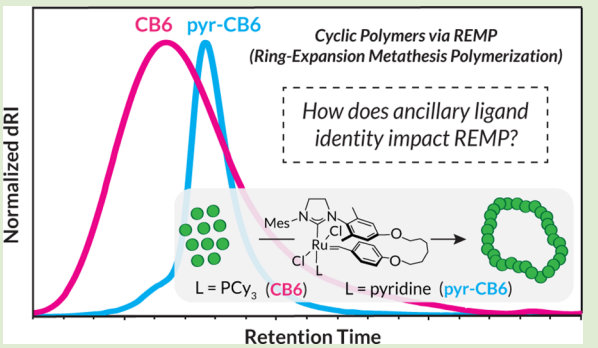
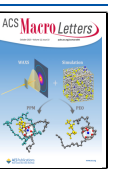
ABSTRACT: The synthesis of well-defined cyclic polymers is crucial to exploring applications spanning engineering, energy, and biomedicine. These materials lack chain-ends and are therefore imbued with unique bulk properties. Despite recent advancements, the general methodology for controlled cyclic polymer synthesis via ring-expansion metathesis polymerization (REMP) remains challenging. Low initiator activity leads to high molar mass polymers at short reaction times that subsequently "evolve" to smaller polymeric products. In this work, we demonstrate that *in situ* addition of pyridine to the tethered ruthenium-benzylidene REMP initiator **CB6** increases ancillary ligand lability to synthesize controlled and low dispersity cyclic poly(norbornene) on a short time scale without relying on molar mass evolution events.



The utilization of macrocyclic templates to initiate ring-expansion polymerizations enables access to myriad cyclic polymers[1−9] imbued with unique solution-state and bulk physical properties compared to their acyclic analogs.[10−16] The synthesis of cyclic polymers via ring-expansion polymerization[17,18] is more convenient than ring-closure of functionalized linear polymers,[19] because REP initiators simultaneously control both insertion and ring closure. Inspired by the growing popularity of ring-opening metathesis polymerization (ROMP) methodologies[20−33] to synthesize linear macromolecules with complex sequences and rich functionalities, ring-expansion metathesis polymerization (REMP)[34−38] methodologies aim to expand the scope of analogous cyclic macromolecules and the ease by which they are made. The evolution of organometallic (e.g., Ru, W, Mo) REMP initiators[36,37,39−48] has lagged compared to the advancements made in ROMP initiator development, likely due to the difficulties associated with synthesizing the former and analytical challenges in characterizing[11,49] putative cyclic macromolecules.

For example, despite decades of work by Schrock on tungsten-based ROMP initiators,[22,23,31,33,50] only in recent years has REMP using W-based initiators emerged as a promising strategy to access a diverse array of materials, including cyclic poly(norbornene)s[45,51] and cyclic poly(acetylene)s.[44,46,52−54] Although cyclic variants of the popularized Grubbs-type Ru initiators (e.g., Grubbs second generation, **G2**;[26,55−57] Figure 1A), developed by Fürstner[41,58] and Grubbs,[36,37,42,43] emerged over a decade ago (e.g., **UC5**, Figure 1B), they were plagued with structural instability and poor molar mass control due to less sterically demanding *N*-heterocyclic carbene (NHC) ligands and Ru-alkylidene moieties, respectively. Compared with the history of **G2**, complexes such as **UC5** have not been fully optimized for the controlled synthesis of cyclic polymers. In response to this shortcoming, our group recently reported on the synthesis of a homogeneous cyclic Ru-NHC initiator following similar design principles as **G2**; **CB6** (Figure 1B) features a bulky diaryl NHC ligand and a Ru-benzylidene.[38,59] As a result, **CB6** is a more stable organometallic complex that offers improved control over molar mass and expedited propagation kinetics compared to the former state-of-the-art initiators (e.g., **UC5**). Nonetheless, REMP with **CB6** still requires extended reaction times due to molar mass evolution; secondary metathesis decreases the polymer molar mass via chain transfer,[43] producing cyclic products with broad dispersity ($Đ$ = ca. 1.5). While utilizing an initiator with a more labile ancillary ligand than PCy_3 (e.g., pyridine) improves molar mass control via increased initiation rates (k_i),[28] such principles have not been applied to REMP. Herein, we demonstrate that well-defined cyclic polymers are readily accessible from a **CB6** scaffold upon *in situ* ligand exchange with pyridine (Figure 1C); the resulting initiator affords cyclic polymers on shorter time scales alongside decreased $Đ$. Importantly, molar mass control is not reliant on chain transfer events following ring closure.

Received: August 29, 2023
Accepted: September 6, 2023
Published: September 11, 2023



https://doi.org/10.1021/acsmacrolett.3c00520
ACS Macro Lett. 2023, 12, 1286−1292

Before exploring conditions for ancillary ligand exchange, we readdressed the synthesis of **CB6** to avoid the generation of sensitive intermediates. Our previous report[38] detailed the generation of a chloroform-protected NHC-adduct that proved to be capricious on a larger scale and when stored for extended periods of time. Following the synthesis of the aryl bromide **1** and amination under revised conditions (12 mol % Pd-PEPPSI-IPr)[60] to give compound **2**, subsequent cyclization under acidic conditions affords imidazolium chloride salt **3**. The advanced imidazolium chloride salt **3** can be stored in a benchtop desiccator without any observable decomposition for at least 12 months (Figure S7). We directly treated **3** with sodium hydride for 16 h and then Grubbs first generation (**G1**) for 1.5 h to promote NHC ligand exchange. Then, we diluted (2 mM) and heated (70 °C) the reaction mixture to induce cyclization and yield our target initiator, **CB6** (Scheme 1).

Interestingly, although **CB6** was the major species isolated after triturating the crude reaction mixture with pentane, it was contaminated with 11% of a minor Ru−benzylidene complex not previously observed. Isolation of an analytically pure sample of the minor impurity by preparative gel permeation chromatography (GPC) reveals a similarity between the two Ru-species' ^{1}H and ^{13}C NMR spectra (Figures S9−S13), but a molar mass roughly twice that of **CB6**,[61] as evidenced by high-resolution mass spectrometry (Figures 2A and S25−S27). Combined, these data support the formation of a dimeric **CB6** species, **bis-CB6**, during the ligand exchange step. While **CB6** and **bis-CB6** do not interconvert between one another at elevated temperatures (Figure S14), room temperature equilibration between the uncyclized analogs (i.e., immediately following addition of **G1**) increases the ratio of **bis-CB6**/**CB6** at extended reaction times (Figure S15); shorter ligand exchange times lead to incomplete **G1** conversion (Figure S16). Furthermore, the absence of an upfield benzylidene resonance with observable $^{4}J_{P,H}$ rules out the presence of the *cis* chloride ligands necessary to form a (μ-dichloro)dimer (Figure S11).[62] It was found that REMP initiation of an emblematic *exo*-norbornene imide monomer, **AcNb**, ([**AcNb**]$_0$/[**I**]$_0$ = 200:1) with pure **bis-CB6** leads to poor control over molar mass relative to **CB6** initiation (M_n = 299 kDa for **bis-CB6** vs 140 kDa for **CB6**, 21 h, Table S1), likely due to twice as many Ru-benzylidene per initiator. Strict removal of **bis-CB6** contamination from **CB6** is not required for efficient REMP, however; minimal differences in GPC traces were observed between REMP initiated with pure **CB6** versus REMP initiated with 8:1 **CB6**/**bis-CB6** (Figures 2B, S28, and S29, and Table S1).

With a more robust synthesis of **CB6** in hand, we turned our attention toward improving REMP molar mass and $Đ$ control by tuning the identity of the ancillary ligand. In ROMP, exchanging PCy_3 (**G2**) for more labile pyridine ligands (Grubbs third generation, **G3**) increases the rate of initiation (k_i) relative to the rate of monomer propagation (k_p), and living characteristics are observed.[28] Unlike ROMP, however, to date, Ru-mediated REMP is reliant on intramolecular chain-transfer (i.e., backbiting) to form the final macrocycle product. Hence, even if narrowly dispersed ring-expanded intermediates were obtained, it is unclear how the nature of this organometallic intermediate would impact the composition of the cyclic polymer products during ring closure.

Treatment of **CB6** with excess pyridine (ca. 100 equiv) for 15 min afforded an isolable dark green solid **pyr-CB6** akin to **G3**. This complex, **pyr-CB6**, proved to be capricious in our hands, however, and was short-lived once isolated; it decomposed within 24 h, as assessed by ^{1}H NMR spectroscopy, even when stored under an inert atmosphere at ca. −20 °C (Figure S21). To

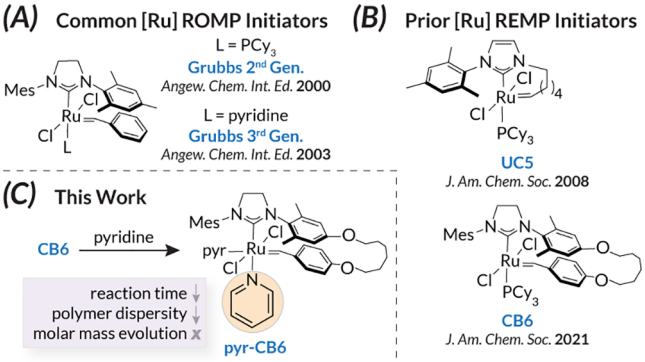
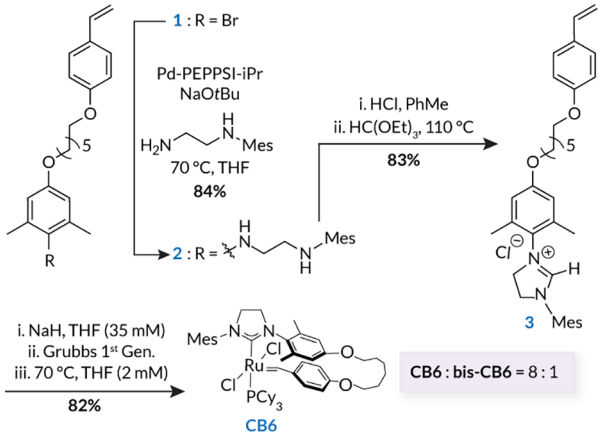


Figure 1. Structures of established Ru-based (a) ROMP and (b) REMP initiators alongside REMP initiator developments reported in (c) this work.

Scheme 1. Revised Synthesis of REMP Initiator CB6



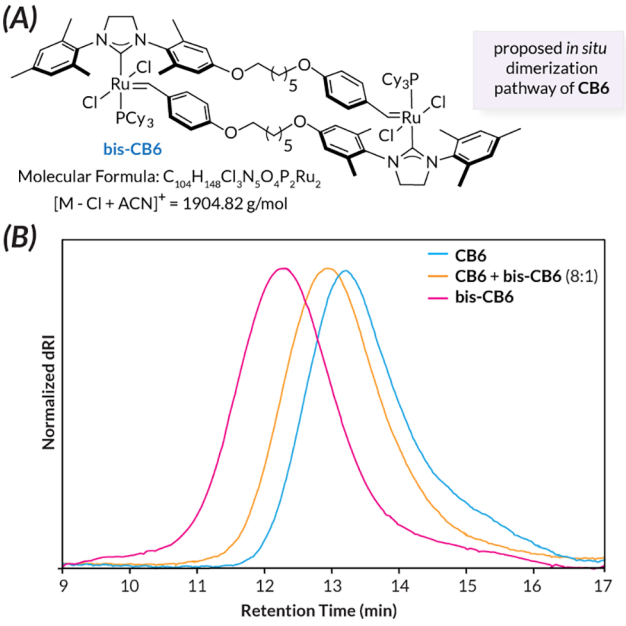


Figure 2. (a) Proposed structure of the minor product from the updated **CB6** synthetic route, **bis-CB6**; (b) The presence of 11% **bis-CB6** does not have significant consequences on subsequent **AcNb** REMP, as assessed by GPC.

https://doi.org/10.1021/acsmacrolett.3c00520
ACS Macro Lett. 2023, 12, 1286−1292

overcome this stability issue, we hypothesized that we could generate a similar species to **pyr-CB6** *in situ*[63] by treating **CB6** with excess pyridine; the resulting solution should initiate faster than **CB6** once added directly to monomer solutions for subsequent REMP (Figure 3A). Treatment of **AcNb** with various [**CB6**]/[pyridine] ratios at 55 °C afforded narrowly dispersed GPC traces at higher [pyridine] (32 equiv) in just 1 h (Figure 3B and Tables 1 and S2). Quenching REMP reactions with ethyl vinyl ether should lead to a change in topology (i.e., cyclic to acyclic) if Ru-containing macrocycles have not yet backbitten. After 1 h reaction time, we do not observe any differences between unquenched and quenched samples as assessed by GPC coupled to multiangle light scattering (GPC-MALS) (Figure S33), indicating that backbiting has occurred, at least within our detection limits.

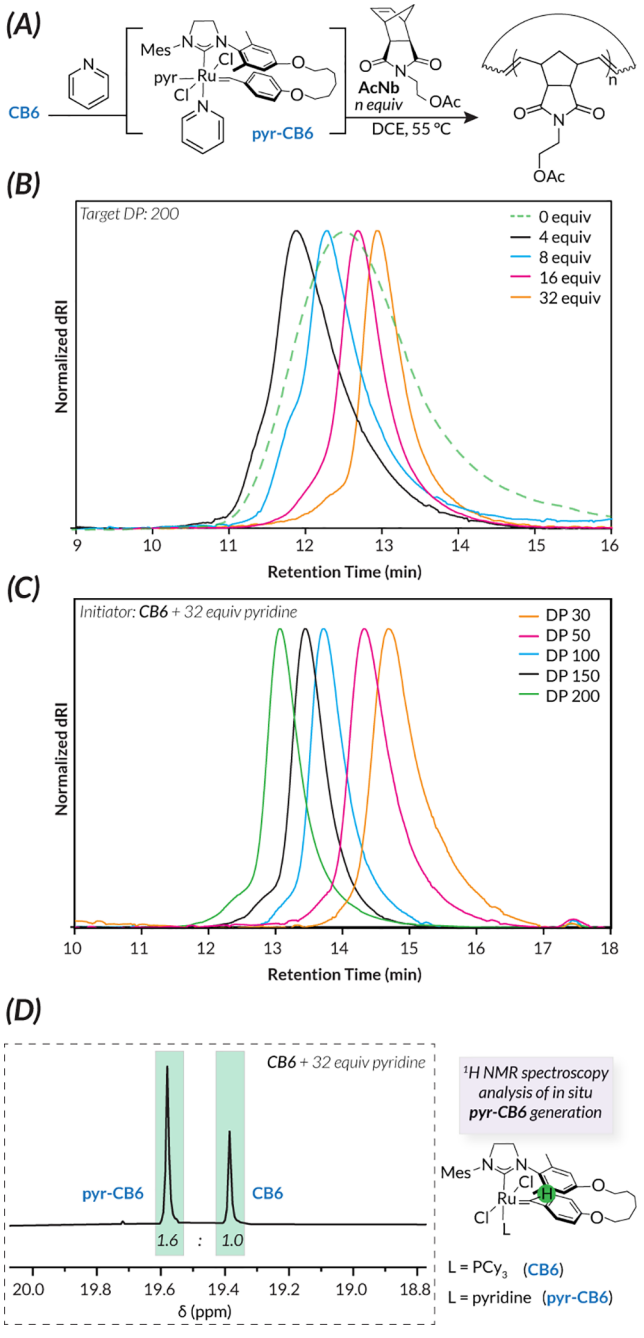


Figure 3. (a) *In situ* formation of **pyr-CB6** for REMP; REMP GPC traces as a function of (b) pyridine equivalency and (c) target DP: REMP reaction initiated with **CB6** (0 equiv pyridine) was run for 21 h, REMP reactions initiated with **pyr-CB6** were run for 1 h; (d) ^{1}H NMR spectroscopy characterization of *in situ* generated **pyr-CB6**.

Table 1. REMP of AcNb Initiated by pyr-CB6[a]

$[M]_0/[I]_0$	equiv. pyridine	$M_{n,theor}$ (kDa)	M_n[c] (kDa)	$Đ$[c]
200:1	0[b]	49.9	140	1.56
200:1	4	49.9	375	1.11
200:1	8	49.9	264	1.09
200:1	16	49.9	170	1.07
200:1	32	49.9	135	1.05
30:1	32	7.49	15.8	1.05
50:1	32	12.5	24.4	1.02
100:1	32	25.0	53.9	1.05
150:1	32	37.4	77.0	1.03

[a]Polymerization reactions were stirred at 55 °C in DCE for 1 h, sealed under nitrogen. [b]REMP reaction initiated without pyridine was stirred at 55 °C in DCE for 21 h, sealed under nitrogen. [c]Measured by GPC-MALS-IV-RI ($CHCl_3$, 35 °C).

At lower pyridine concentrations, broadening in the GPC traces approached those observed with **CB6**. As demonstrated by Guironnet, increasing concentrations of excess pyridine decreases the rate of monomer consumption in **G3** initiated ROMP.[64] In our REMP system, while a minimum concentration of pyridine is necessary to displace PCy_3, we opted for the lowest effective concentration (32 equiv) to avoid potential adverse consequences on the reaction rates. Cyclic architecture was first evaluated by comparing the retention times of a REMP polymer and an acyclic ROMP polymer with similar M_w and $Đ$ values using GPC-MALS. Consistent with an architectural difference, despite having similar molar masses (M_w = ca. 140−150 kDa), the REMP sample has a longer GPC retention time (Figure S30). Furthermore, the absolute molar masses of several REMP samples were compared to that of a broadly dispersed ROMP polymer (Table S6); REMP molar masses were consistently higher than the ROMP molar masses at a given retention time (Figures S31). These combined observations are consistent with cyclic polymers being denser than their acyclic counterparts and thus appearing "smaller" than expected in solution. Further analysis was performed using GPC-MALS coupled to an intrinsic viscometry (IV) detector. A lower intrinsic viscosity for the REMP samples compared to the ROMP sample (i.e., $[\eta_{cyclic}] < [\eta_{linear}]$),[10,18,35] as assessed by a Mark−Houwink−Sakurada analysis (Figure S32), further corroborates the topological assignments. While a variety of $[\eta_{cyclic}]/[\eta_{linear}]$ has been reported in the literature,[5,6,16,44,46,49,54,65−67] in this case, $[\eta_{cyclic}]/[\eta_{linear}]$ = ca. 0.85−0.88, which is consistent with our previous findings from REMP of **AcNb** with **CB6**.[38] Importantly, ^{1}H NMR spectroscopy analysis (Figures S22−S24) confirms that backbone stereochemistry is comparable among all REMP and ROMP samples (ca. 40−50% *trans* olefin).

Next, we evaluated the impact of ancillary ligand identity on a REMP reaction profile at different degrees of polymerization (DP). **AcNb**, with **pyr-CB6** at various feed ratios (30:1−200:1, Figure 3C), afforded a series of narrowly dispersed polymers ranging from 375 kDa ($Đ$ = 1.11) to 133 kDa ($Đ$ = 1.05) after 1 h (Tables 1 and S4) with an increase in M_n that tracks with increasing $[M/I]_0$.

Although we observed qualitative improvements to our REMP methodology by initiating with an unpurified mixture of **CB6** and pyridine, we were uncertain about the actual identity

https://doi.org/10.1021/acsmacrolett.3c00520
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of active initiator(s) in solution. As assessed by ^{1}H NMR spectroscopy, a solution of **CB6** + pyridine (32 equiv) consists of a 1.6:1 mixture of **pyr-CB6** and **CB6** (PCy_3 ancillary ligand), as evidenced by two Ru-benzylidene resonances at ca. 19−20 ppm (Figures 3D and S17).[64] In other words, about 60% of Ru-containing species in solution are ligated by pyridine. These data are corroborated with ^{31}P NMR spectroscopy evidence for free PCy_3 (i.e., **pyr-CB6**, 9.55 ppm) and ligated PCy_3 (i.e., **CB6**, 28.5 ppm) in solution (Figure S18) in a 1.3:1 ratio, which is in agreement with the **pyr-CB6** population observed by ^{1}H NMR spectroscopy. Furthermore, an analogous mixture is formed when **G2** is treated with excess pyridine (32 equiv); ^{1}H NMR spectroscopy reveals two Ru-benzylidene resonances, while ^{31}P NMR spectroscopy shows the presence of both free and bound PCy_3 (Figures S19 and S20) in similar ratios as to what was observed for **CB6**.

Interestingly, the cyclic polymers generated from **pyr-CB6** initiation show virtually no change in molar mass between 15 min and 21 h of reaction time (Figures 4A and S34 and Table S3). This observation is in stark contrast to the molar mass evolution profiles observed following **CB6** or macrocyclic Ru-alkylidene (e.g., **UC5** or **SC5**) REMP initiation.[37,38,43] Typically, Ru-initiated REMP generates high molar mass polymers at short reaction times; the molar mass profile evolves with extended reaction times, as inter- and intramolecular chain transfer (i.e., secondary metathesis) between growing macrocycles and other cyclic polymers leads to a reduction in average chain length (Figure 4B). It is believed that this molar mass evolution process *resembles* the equilibration toward a single thermodynamic product (i.e., macrocycle size), but the dependence of the final molar mass on the feed ratio and initiator identity suggests that orthogonal processes (e.g., initiator death) also contribute to the overall evolution process.[43] As a result, in the case of **CB6**, there is a loose correlation between the feed ratio and final molar mass at extended reaction times following molar mass evolution. When REMP is initiated with **pyr-CB6**, however, the initial cyclic products not only fail to undergo molar mass evolution, but also their M_n approximate of those formed via **CB6** initiation at longer reaction times (Figure 4C). In other words, similar cyclic polymer products are generated independent of initiator identity, but **pyr-CB6** facilitates their almost immediate formation without the need for intermolecular chain transfer equilibration events. We envision that an increased k_i for REMP mediated by **pyr-CB6** leads to more uniform ring expansion (i.e., smaller metallocycles) and ultimately a higher likelihood of yielding lower molar mass polymers during backbiting. Interestingly, when we resubjected a purified REMP polymer (M_n = 24 kDa) to freshly prepared **pyr-CB6** for 1 h at 55 °C, no observable change in the GPC-MALS-RI data (Figure S35) was noted, suggesting that, evidently, when *in situ* generated **pyr-CB6** is used, backbiting (i.e., *intramolecular* chain transfer) can occur, but *intermolecular* chain transfer appears inoperative. Overall, the REMP initiated by **pyr-CB6** provides a framework that improves upon the molar mass control and precision by which cyclic polymers are synthesized using ring-expansion polymerization methodologies.

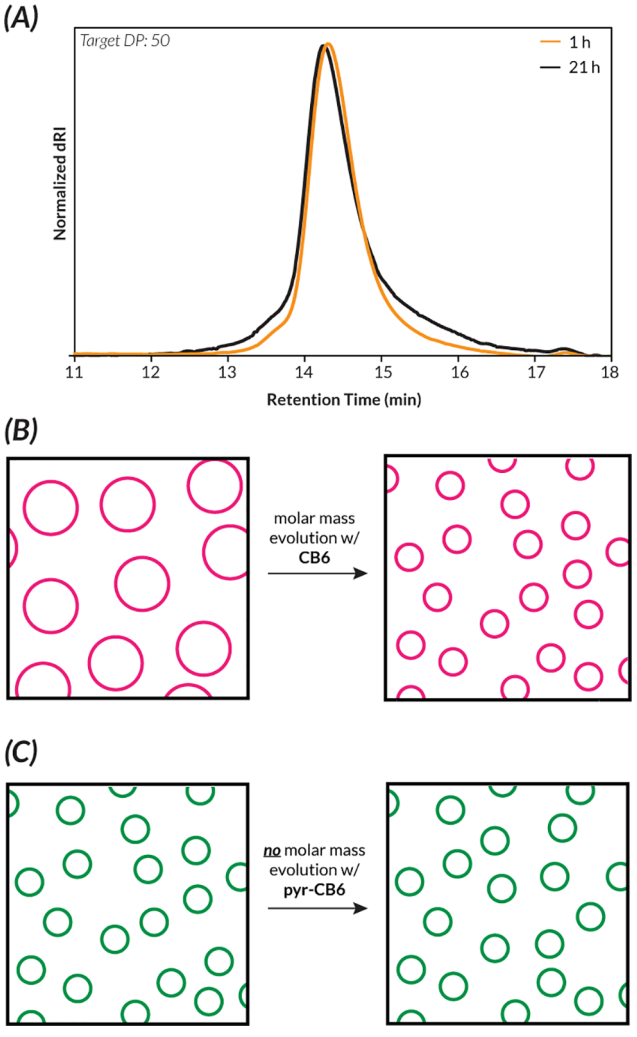

Figure 4. (a) GPC traces of REMP reactions initiated with **pyr-CB6** over time; overview of REMP molar mass evolution process with (b) **CB6** and (c) **pyr-CB6**.

The combined REMP GPC and NMR spectroscopy data suggest that while only ca. 60% of [Ru] in solution is ligated by pyridine, this **pyr-CB6** species initiates significantly faster than **CB6**. Based on the large polymers formed with **CB6** at early time points, it is likely that **CB6** has a relatively low initiator efficiency.[38] The overall initiator efficiency can be increased through the *in situ* formation of **pyr-CB6**, even if some **CB6** remains in solution. It is hypothesized that the faster initiation of **pyr-CB6** dominates at early reaction times and ultimately dictates the reaction profile; more growing polymer chains lead to smaller polymers than when **CB6** alone is used, circumventing the need to rely on molar mass evolution via secondary metathesis (*vide supra*). If one considers that ca. 60% of the initiator solution is significantly more active (i.e., **pyr-CB6**) than the remaining phosphine-ligated **CB6**, it is reasonable that $[M/I]_0$ (Table 1) values should actually be larger (i.e., target molar masses are higher than expected) and that there is even better experimental agreement between M_n and $M_{n,theor}$ (Table S5) than expected (Tables 1 and S4). For example, when taking these adjustments into consideration, $[M/I]_0$ = 50:1 ($M_{n,theor}$ = 12.5 kDa) is actually $[M/I]_0$ = 83:1 ($M_{n,theor}$ = 20.8 kDa; Table S5); the latter is more consistent with experimental M_n = 24.4 kDa.

In summary, we have outlined an expedited method to access the **CB6** REMP initiator and implemented a protocol to refine the cyclic polymer molar mass control. The updated synthesis of **CB6** relies on a direct conversion of imidazolium **3** to **CB6** in one pot under basic conditions. In the process, a small amount (11%) of dimeric **CB6**, **bis-CB6** is formed, but it was determined that its presence has minimal impact on REMP.

https://doi.org/10.1021/acsmacrolett.3c00520
ACS Macro Lett. 2023, 12, 1286−1292

We then demonstrated that while **pyr-CB6**, a cyclic analogue of the more active ROMP initiator **G3**, has a short lifetime in the solid state, a similar species can be generated *in situ* by the addition of pyridine to **CB6**. The overall result is the controlled synthesis of cyclic polymers at short reaction times devoid of extensive molar mass evolution events. These collective findings will allow for the synthesis of more complex cyclic polymers (e.g., multiblock architectures) due to the increased structural control gained from this improved methodology.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00520.

General experimental procedures and characterization, NMR data, GPC traces, and conglomerate GPC-MALS-IV-RI data (PDF)

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‡These authors (A.M.L. and C.M.M.) contributed equally. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): T-W.W. and M.R.G. are inventors on Patent Application PCT/US2022/023353.

■ ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under CHE-2142922 and generous startup funds from the University of Washington. A.M.L and C.M.M. acknowledge the University of Washington Clean Energy Institute for graduate research fellowships. NMR instrumentation is supported under NIH S10 OD030224-01A1. Umicore is thanked for a generous gift of Grubbs first generation catalyst. Dr. Martin Sadilek is acknowledged for assistance with HRMS experiments.

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