# Strategies to Enhance Cyclopolymerization using Third-Generation Grubbs Catalyst

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S *Supporting Information*

ABSTRACT: Cyclopolymerization (CP) of 1,6-heptadiyne derivatives using the Grubbs catalysts has been known to afford conjugated polyenes in low yields in dichloromethane (DCM), the most common solvent for olefin metathesis polymerization and a good solvent for typical conjugated polymers. Based on our previous work that showed highly efficient CP using the Grubbs catalysts in tetrahydrofuran (THF), we developed a new polymerization system using weakly coordinating additives with the third-generation Grubbs catalyst in DCM. The polymerization efficiency of various monomers and their controls dramatically increased by adding 3,5-dichloropyridine, yielding polymers with narrow polydispersity indices (PDIs) at low temperatures. These new reaction conditions not only expand the monomer scope by resolving the solubility concerns of conjugated polymers but also more effectively reduced the chain transfer. Consequently, fully conjugated diblock copolymer was successfully prepared. Additionally, kinetic analysis has revealed that low CP efficiency in DCM resulted from the rapid decomposition of the propagating carbene. This decomposition was effectively suppressed by both pyridine additives and THF, suggesting that weakly coordinating additives stabilize the living chain end. Furthermore, we observed that the turnover number of CP was higher at lower temperatures (0−10 °C) than at ambient temperatures, consistent with the understanding that the lifetime of a propagating carbene is greater at lower temperatures. Steric protection was also shown to increase the stability of the propagating carbene, as shown by a higher turnover number for the 3,3-dimethyl-substituted 1,6-heptadiyne compared to the nonfunctionalized monomer.
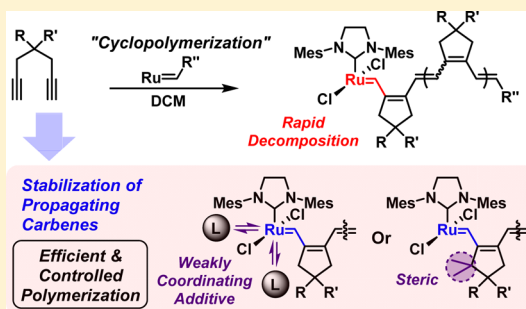
INTRODUCTION

Cyclopolymerization (CP) of 1,6-heptadiyne derivatives via olefin metathesis provides a powerful and easy method for the synthesis of conjugated polyenes,[1] whose utility has increased with recent developments of living polymerization. Early studies of CP were carried out using classical ill-defined catalysts, including Ziegler−Natta,[2−5] MoCl$_5$, and WCl$_6$ and thus provided little understanding of the CP mechanism.[6−11] However, recent work by Schrock and colleagues using well-defined Schrock catalysts has provided a better understanding of the mechanism of CP by examining the effects of catalyst regioselectivity on the structure of the polymer backbone.[12−16] Unfortunately, the common Ru-based Grubbs catalysts have not been effective in catalyzing CP, despite their versatile utility in other olefin metathesis reactions.[17] Because the reactivity of Grubbs catalysts for alkyne polymerization was much lower than that of Mo- or W-based catalysts,[18] Buchmeiser group replaced the X-type ligands on the Grubbs catalysts with stronger electron-withdrawing groups, obtaining greater reactivity for CP and, notably, excellent regioselective control through exclusive α-addition (Scheme 1).[17,19−23] However, the modified initiators mostly showed low k_i/k_p values, making it difficult to prepare conjugated polyenes with low polydispersity indices (PDIs).

Scheme 1. Cyclopolymerization of 1,6-Heptadiyne Derivatives by Grubbs Catalyst
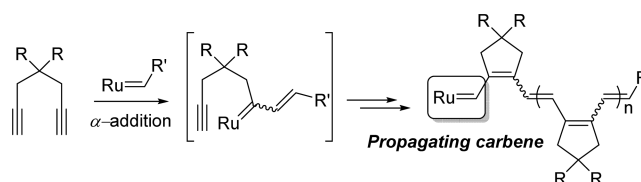
Recently, we reported greatly enhanced reactivity in the CP of 1,6-heptadiyne derivatives using the third-generation Grubbs catalyst[24] and the second-generation Hoveyda−Grubbs catalyst[25] by simply changing the solvent from dichloromethane (DCM) to tetrahydrofuran (THF). This discovery greatly expanded the utility of CP because the Grubbs catalysts not only promoted living polymerization of 1,6-heptadiyne[24] and 1,7-octadiyne derivatives via exclusive α-addition to afford conjugated polymers with narrow PDIs[26,27] but also allowed for the preparation of block copolymers, rod-like molecular wires,[24,25] and nanospheres via direct self-assembly.[28] Despite the advantages of using THF, DCM is still a preferred solvent for CP, because conjugated polymers are generally much more

soluble in chlorinated solvents. For example, diethyl dipropargylmalonate (DEDPM), which is one of the most commonly used monomers for the CP, gives polymer that is insoluble in THF; therefore, we had to replace it by more soluble dihexyl dipropargylmalonate (DHDPM) having longer n-hexyl chain as a substituent.[24] Therefore, the utility and monomer scope of CP would be further broadened if conditions could be developed to achieve living polymerization in DCM.

The greatly enhanced reactivity of the Grubbs catalysts in THF raises the question of why such drastic solvent effects were observed. In the previous report, we proposed that weakly coordinating THF effectively stabilizes the active propagating Ru carbene,[24] suggesting that detailed mechanistic investigations to understand the difference between THF and DCM would be valuable in expanding the utility of CP. Herein we report a new method of efficient living CP using the fast initiating third-generation Grubbs catalyst in DCM by introducing weakly coordinating reagents as an additive, thereby, increasing the CP efficiency for various monomers to afford polyenes with controlled molecular weights and narrow PDIs that had previously been insoluble in THF. Furthermore, we demonstrate how the additive, reaction temperature, and substituents on the monomer affect the lifetime of the active propagating carbene on the growing polymer chain end, and how maximizing this lifetime is crucial for improving the CP efficiency.

■ RESULTS AND DISCUSSION

In 2011, we reported a substantial solvent effect for CP using Grubbs catalysts. DCM, the most widely used solvent for olefin metathesis reactions, was a poor solvent for the CP, whereas the CP by third-generation Grubbs catalyst (**Cat**) in THF showed dramatically improved result; with a monomer-to-initiator ratio (M/I) of 100, conversion of DEDPM (**M1**) was only 18% in DCM, but 92% in THF.[24] This solvent effect was ironic because DCM was the most popular solvents in olefin metathesis reactions using Ru-complexes, particularly in ROMP. Not only many initiators, monomers, and polymers show great solubility in DCM, but also it was reported that DCM stabilized the catalyst.[29,30] Furthermore, huge solvent effect on the metathesis polymerization was less common with exceptions of a few reports on ROMP, demonstrating that solvents affected the control of tacticities,[31] propagation rate,[29] and inhibition of secondary metathesis reaction.[32] In order to use DCM as the polymerization solvent, we investigated on the origin of this huge solvent effect (THF ≫ DCM).[33]

Solvents with high dielectric constants (ε) are known to stabilize four-coordinate, 14 electron−metal complexes after ligand dissociation.[30] However, in our preliminary experiments, diethyl ether ($\varepsilon = 4.34$), a less polar solvent than DCM ($\varepsilon = 8.9$), was also an effective solvent for the polymerization of DHDPM. Therefore, we proposed that the major role of THF and diethyl ether in the polymerization of DHDPM was to act as a weakly coordinating ligand. To investigate the coordination effect more extensively, we ran several CP experiments of **M1** using **Cat** and compared the CP efficiency of various external ligands in DCM while holding the M/I ratio fixed at 50. As a control experiment, **M1** was polymerized without any additive, resulting in 68% conversion at room temperature (Table 1, entry 1). On the other hand, monomer conversion at room temperature increased to 90% upon adding 40 mol % THF (Table 1, entry 3). Because it was difficult to handle very small

Table 1. Additive Screening for Polymerization of DEDPM (M1)

entry	additive	M/I/Add	temp	time	$M_n{}^a$ (g/mol)	PDI^a	conv^b (%)
1	–	50/1/−	RT	1 h	12.6 k	2.56	68
2	–	50/1/−	0 °C	1 h	21.5 k	2.38	90
3	THF	50/1/20	RT	1 h	10.5 k	2.00	91
4	2,6-Cl$_2$BQ	50/1/10	RT	1 h	19.4 k	2.41	89
5	2,6-Cl$_2$BQ	50/1/10	0 °C	1 h	16.4 k	2.11	98
6	3,5-Cl$_2$Py	50/1/10	RT	1 h	26.4 k	1.13	>99
7	3,5-Cl$_2$Py	100/1/20	RT	1 h	39.7 k	1.62	90
8	3,5-Cl$_2$Py	100/1/20	10 °C	3 h	49.9 k	1.16	91

^{a}Determined by CHCl$_3$ SEC calibrated using polystyrene (PS) standards. ^{b}Calculated from ^{1}H NMR.

amounts of liquid THF, we screened solid reagents as alternative additives. The first candidate was benzoquinone because it is known to inhibit the decomposition of Grubbs catalyst.[34] Adding 20 mol % of 2,6-dichlorobenzoquinone (2,6-Cl$_2$BQ) increased the conversion to 89% (Table 1, entry 4). However, in all the preceding cases, the PDIs of the resulting polymers were still very broad (>2), leading us to speculate that the high catalyst activity resulted in an extensive chain transfer. Lowering the reaction temperature to 0 °C to suppress the chain transfer reaction,[24] proved largely ineffective (Table 1, entry 5). Interestingly, we found that lowering the reaction temperature could also increase the monomer conversion (Table 1: entry 1 vs 2 and entry 4 vs 5), an initially counterintuitive finding given how temperature increase generally results in better activity for olefin metathesis. This observation will be discussed further when we review our findings from kinetic analysis.

Assuming that the weakly coordinating ketone functionality of 2,6-Cl$_2$BQ might be responsible for the observed improvement in polymerization, we tested another solid reagent, 3,5-dichloropyridine (3,5-Cl$_2$Py), as a substitute for liquid 3-chloropyridine, a labile ligand already bound to **Cat**. Adding 20 mol % of 3,5-Cl$_2$Py led to the full conversion of **M1** to polymer in 1 h at room temperature, with a surprisingly narrow PDI of 1.13 (Table 1, entry 6). Increasing M/I to 100 led to high conversion of **M1** at room temperature, along with significantly broadening the PDI. Lowering the reaction temperature to 10 °C suppressed the chain transfer and successfully reduced the PDI from 1.62 to 1.16 (Table 1, entries 7 and 8), demonstrating that not only conversion can be improved but also controlled polymerization can be achieved by adding the appropriate additive in the DCM solvent system.

M1 and several other 1,6-heptadiyne derivatives were tested for controlled CP under the optimized reaction conditions (20 mol % of 3,5-Cl$_2$Py) (Figure 1). Various monomers (**M1−M4**) were successfully polymerized in a controlled manner to afford polymers with molecular weights directly proportional to the
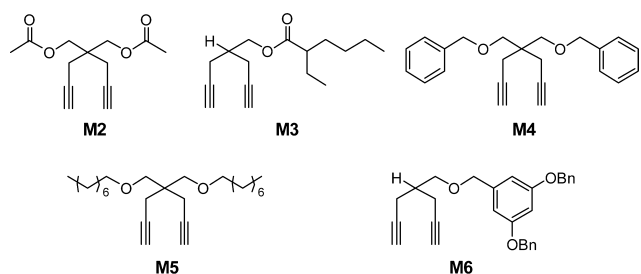
Figure 1. Various monomers used for controlled polymerization.

Figure 2. Plots of M_n vs M/I and corresponding PDI values for poly(M1) through poly(M4). The actual M/I values were calculated from the initial feeding ratios and the final conversions.

M/I ratio and with narrow PDIs in the range 1.08−1.31 (Table 2 and Figure 2, and see Figure S1). In our previous work in THF,[24,25] we could only use monomers containing long alkyl groups or bulky moieties to overcome the solubility problems of typical conjugated polyenes. Now, with the improved solubility in DCM, monomers containing short side chains (M1 and M2) could yield polymers with high M_n values (up to 50 k) and narrow PDIs (Table 2, entries 1−9; Figure 2a,b). Polymerization of monosubstituted ester M3 in THF (M/I = 100) resulted in a broad PDI (2.23), even at −10 °C, because a relatively small side-chain could not effectively suppress the chain transfer. In contrast, with 20 mol % of the pyridine additive, CP of M3 in DCM at 0 °C produced polymers with a high degree of polymerization (DP) of 200 and narrow PDIs (Figure 2c and Table 2, entries 10−15). This demonstrated that the new DCM reaction conditions with the right additive could provide better control than the THF conditions. Controlled polymerization was also possible with ether-containing M4, demonstrating an even greater monomer scope (Figure 2d and Table 2, entries 16−19). Meanwhile,
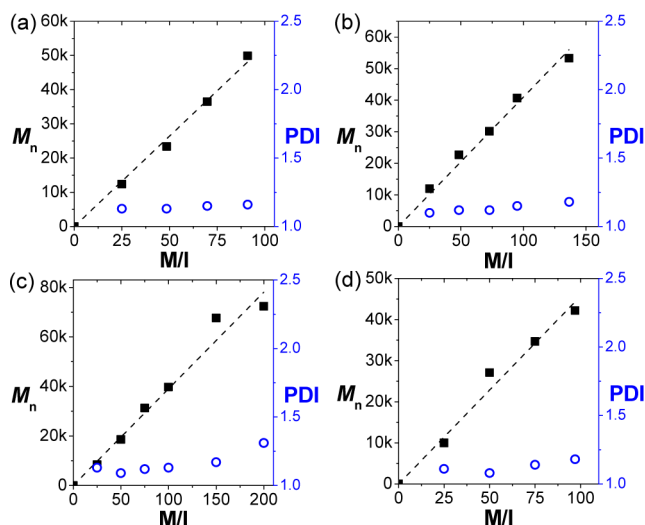
M5, which had previously been polymerized using Schrock catalysts to yield polymers with a broad PDI (2.4),[35] yielded polymers with a much narrower PDI (1.26) using the new DCM system (Table 2, entry 20). The new conditions were even capable of polymerizing M6 to yield low-PDI polymer containing first-generation Fréchet-type dendron,[36] which, while soluble in DCM, exhibited low solubility in THF (Table 2, entry 21). In brief, the use of coordinating additives in DCM has significantly expanded the monomer scope of the controlled CP.

Table 2. Polymerization of Various Monomers

entry	monomer	M/I/Add	temp (°C)	time (h)	$M_n{}^a$ (g/mol)	PDI^a	conv^b (%)
1	M1	25/1/5	10	3 h	12.4 k	1.13	>99
2	M1	50/1/10	10	3 h	23.4 k	1.13	97
3	M1	75/1/15	10	3 h	36.5 k	1.15	93
4	M1	100/1/20	10	3 h	49.9 k	1.16	91
5	M2	25/1/5	10	3 h	12.0 k	1.10	>99
6	M2	50/1/10	10	3 h	22.7 k	1.12	97
7	M2	75/1/15	10	3 h	30.2 k	1.12	97
8	M2	100/1/20	10	3 h	40.7 k	1.15	95
9	M2	150/1/30	10	3 h	53.3 k	1.18	91
10	M3	25/1/5	0	0.5 h	8.4 k	1.13	>99
11	M3	50/1/10	0	1 h	18.6 k	1.09	>99
12	M3	75/1/15	0	1.3 h	31.3 k	1.12	>99
13	M3	100/1/20	0	3 h	39.8 k	1.13	>99
14	M3	150/1/30	0	3 h	67.7 k	1.17	>99
15	M3	200/1/40	0	3 h	72.4 k	1.31	>99
16	M4	25/1/5	10	1.5 h	10.0 k	1.11	>99
17	M4	50/1/10	10	2 h	27.1 k	1.08	>99
18	M4	75/1/15	10	2.5 h	34.7k	1.14	>99
19	M4	100/1/20	10	3 h	42.2 k	1.18	97
20	M5	50/1/10	10	3 h	28.3 k	1.26	>99
21	M6	50/1/10	10	3 h	28.5 k	1.17	99

^{a}Determined by CHCl$_3$ SEC calibrated using polystyrene (PS) standards. ^{b}Calculated from ^{1}H NMR.

To show that living CP is possible in DCM, block copolymerization was attempted. Fully conjugated diblock copolymer was successfully prepared from 50 equiv of **M3** (with respect to catalyst loading) in DCM at 0 °C followed by the addition of 100 equiv of **M2** at 10 °C to produce poly(**M3**)-*b*-poly(**M2**) in 89% isolated yield (Figure 3a). Block
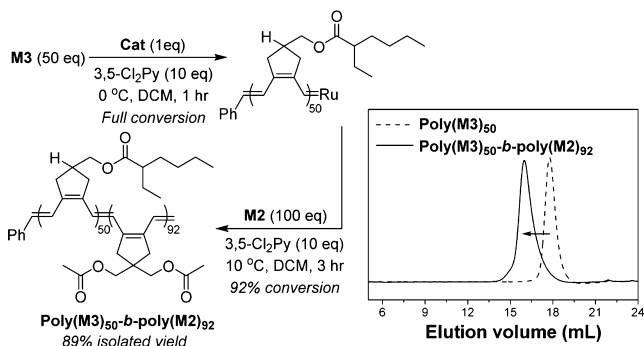

Figure 3. Block copolymerization of **M3** and **M2** in DCM and SEC traces for poly(**M3**)$_{50}$ (M_n = 17.5 k, PDI = 1.11) and poly(**M3**)$_{50}$-*b*-poly(**M2**)$_{92}$ (M_n = 56.2 k, PDI = 1.29).

copolymerization was confirmed using SEC, which revealed an increase in M_n from 17.5 k to 56.2 k upon adding a second monomer; narrow PDIs (<1.3) were successfully maintained throughout the process (Figure 3b). These conditions were more efficient than those of our previous work, because they allowed the doubling of the DP for each block.[24]

To understand how additives improve the CP, we designed ^{1}H NMR experiments to observe how additives affect the propagating carbene and overall conversion. We began by determining the chemical shift of the propagating carbene, mixing a 10:1 ratio of **M1** and **Cat** in DCM-d_2 and obtaining the ^{1}H NMR spectra after full conversion (Figure 4a, (i) and (ii)). The initial benzylidene moiety in **Cat** was observed at 19.1 ppm; upon adding **M1**, new propagating carbenes began to appear at 19.8 ppm. Similarly, with the pyridine additive, the chemical shift for the carbene changed from 19.1 to 19.7 ppm upon the addition of **M1** (Figure 4a, (iv)). Based on these assignments, it becomes possible to monitor changes in the total propagating carbene signals over time by plotting time vs percentage of the remaining propagating carbene (carbene%). Initially, we monitored the carbene signals for the CP of **M1** with M/I = 10 at room temperature without additives; as shown in Figure 4b, carbene% drastically declined early in the reaction before leveling out at less than 50% of the initial carbene concentration (black line). However, we observed much higher carbene% of up to 80% remaining for an otherwise identical reaction with 3,5-Cl$_2$Py added (red line). Moreover, almost no change in carbene% occurred during reaction in deuterated THF (THF-d_8) (blue line). At this point, it is unclear how the propagating carbene decomposes, but it does appear as though weakly coordinating species such as pyridine additives or THF suppress or retard this process.

To understand how decay of the signals for the propagating carbenes affects the CP, both the carbene% and monomer conversion (**M1**) under different reaction conditions were monitored by ^{1}H NMR in DCM-d_2. For CP with M/I = 10 in DCM-d_2 at room temperature, monomer conversion was quite fast (90% after 5 min) even though only half of the propagating carbenes remained (Figure 5a). When the M/I ratio was
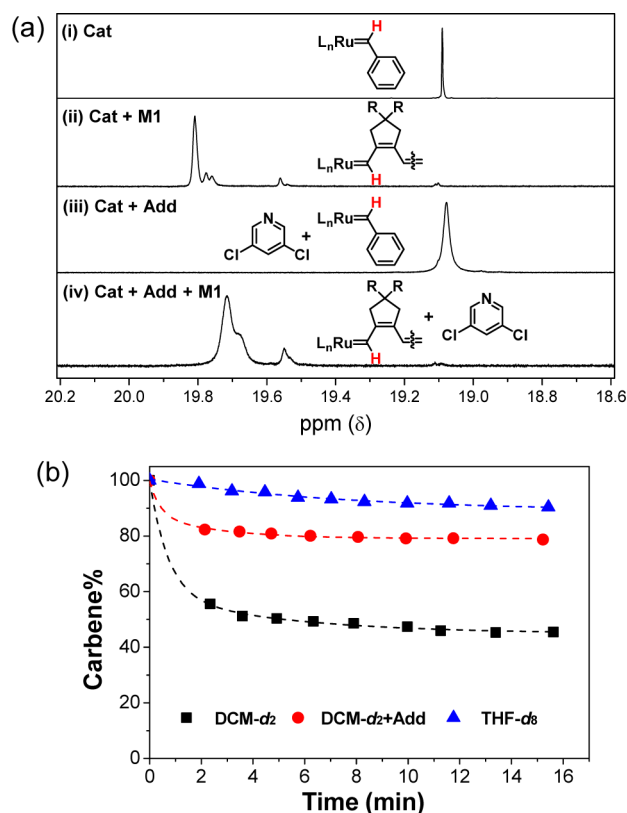

Figure 4. (a) ^{1}H NMR spectra of the initial and propagating carbene of **Cat** and **Cat** + additive in DCM-d_2. (b) Decrease in the carbene signal over time during CP (M/I = 10). Remaining carbene% was calculated from ^{1}H NMR using hexamethyl disilane as an internal standard.

increased to 20, only 10% remained, despite full conversion (Figure 5b). Unfortunately, further comparison using higher M/I ratios was challenging, as monitoring the signal with such a low concentration of propagating carbenes by ^{1}H NMR became more difficult; nevertheless, the data in Figures 5a and 5b suggest that faster decay of the propagating carbene would be observed for higher M/I ratios. This might explain the low conversions of **M1** discussed previously (68% for M/I = 50 and 18% for M/I = 100). On the other hand, carbene% was far greater when 3,5-Cl$_2$Py was added to a reaction where M/I = 10 (Figure 5a vs 5c). Although addition of the external ligand slowed the propagation (90% conversion after 25 min), consistent with how Grubbs catalyst follows a dissociative mechanism,[30] the lifetime of the propagating carbene greatly increased. Consequently, significantly higher turnover numbers were observed for various monomers (Table 2).

While optimizing the reaction conditions, we observed an interesting temperature effect whereby the CP of **M1** proceeded more efficiently at 0 °C than at room temperature (Table 1, entry 1 vs 2 and entry 4 vs 5). To better understand this effect, an additional kinetic analysis was performed at 0 °C (M/I = 10 in DCM-d_2). Indeed, the propagation rate decreased (80% conversion after 40 min) because of the lower catalytic activity at the lower temperature, but carbene decay slowed to a greater extent (Figure 6), accounting for the unusual effect observed. As a result, this increased carbene stability overwhelmed the lower propagation rate, thereby leading to the higher conversion. These kinetic analyses explain why the Grubbs catalysts have not been utilized for the CP of 1,6-
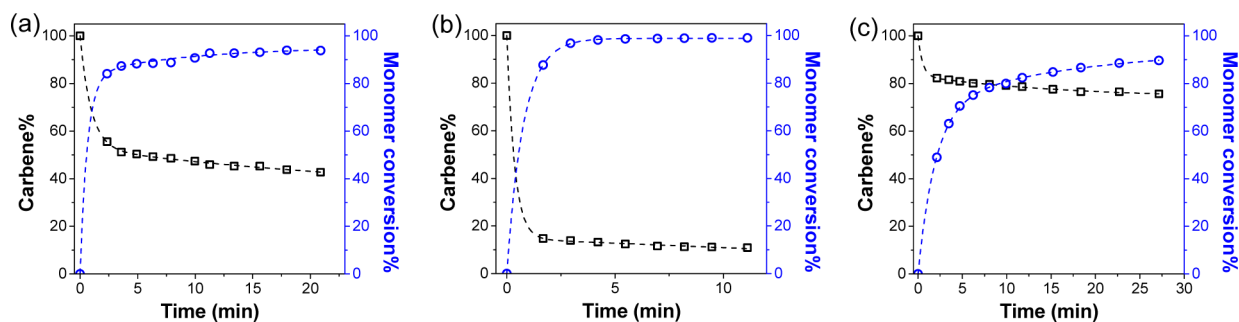
Figure 5. Plots of carbene% and monomer conversion (%) vs time for the CP of **M1** at room temperature for (a) M/I = 10 in DCM-d_2, (b) M/I = 20 in DCM-d_2, and (c) M/I = 10 in DCM-d_2 with the pyridine additive (5 equiv to **Cat I**). Conversions and carbene% were calculated using ^{1}H NMR data.
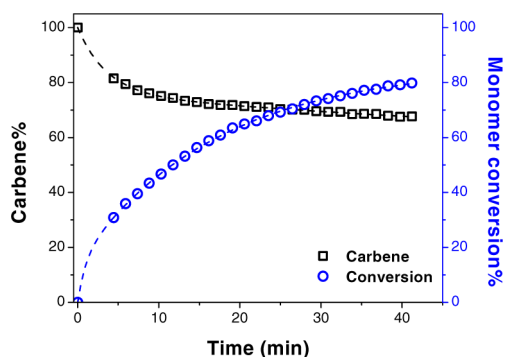
**Figure 6.** Plot of carbene% and monomer conversion (%) vs time for the CP of **M1** for M/I = 10 in DCM-d_2 at 0 °C.

heptadiynes; because the propagating carbenes were not stable enough in DCM at ambient temperature to perform the efficient CP.

Because conversion occurred more slowly at 0 °C, more reliable and insightful kinetic analysis became possible by analyzing the data at the early stages of polymerization. We compared the reaction orders under various polymerization conditions with respect to $-d[M]/dt$ ($[M]$ = concentration of monomer); according to eq 1, any change in $[C]$ (concentration of the initial or propagating carbenes) would strongly affect the order of monomer conversion. Data from the polymerization reactions of **M1** in DCM-d_2, DCM-d_2 + additive, and THF-d_8 at 0 °C reveal that the reaction in THF-d_8 and the reaction in DCM-d_2 with additive follow the first-order kinetics for $[M]$, suggesting ideal living polymerization (Figure 7a,b). However, monomer conversion for the reaction in DCM-d_2 without additive followed at least second-order kinetics, implying a deviation from living polymerization because of significant catalyst decomposition (Figure 7c). These results are also in agreement with the data of Table 1.

$$-\frac{d[M]}{dt} = k_{obs}[M][C] \qquad (1)$$

The use of transition-metal catalysts such as W, Mo, Nb, Ta, and Rh for the synthesis of substituted polyacetylenes from alkynes has been well studied.[37] However, there are far fewer examples of Ru-based Grubbs catalysts being used for this purpose,[38−41] largely because the activity of Grubbs catalysts toward alkyne polymerization (including for CP) has traditionally been believed to be low.[42] Now, it is clear from our mechanistic analysis that the major drawback in the CP of 1,6-heptadiynes is not the lack of intrinsic reactivity between Ru-
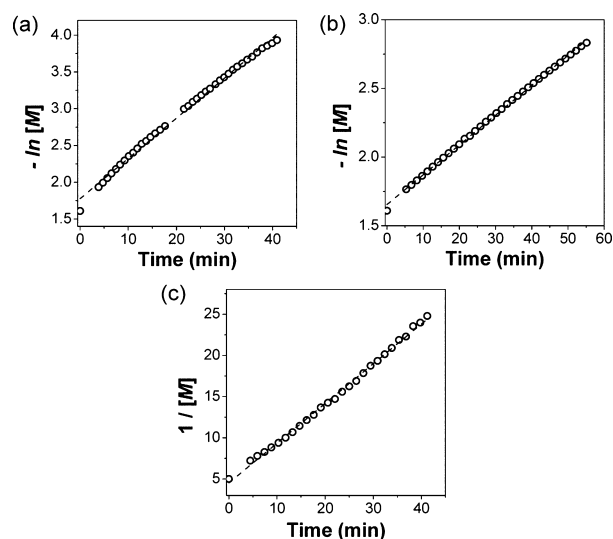
Figure 7. Plots of $-\ln[M]$ vs time for (a) THF-d_8 and (b) DCM-d_2 + additive and (c) $1/[M]$ vs time for DCM-d_2 for CP of **M1** with M/I = 10 at 0 °C.

alkylidenes and alkynes, but rather facile carbene decomposition of the 14-electron Ru-based propagating species that occurs in the absence of external ligands (Figure 8).[43] However, the weakly coordinating external ligands would increase the population of the more stable 18-electron state and the lifetime of the propagating species. (Figure 8) Unsurprisingly, three tested additives (THF, 2,6-Cl$_2$BQ, 3,5-Cl$_2$Py in Table 1) demonstrated this stabilizing effect, as evidenced by the increased monomer conversion. However, the different additives resulted in different PDIs; only 3,5-Cl$_2$Py promoted controlled polymerization to afford polymers with narrow PDIs, presumably because its better coordinating ability also blocked the chain transfer more efficiently. Notably, **M3**, whose polymerization is usually accompanied by a rapid chain transfer reaction, can be polymerized in living manner.

Our discovery on the effect of the stability of propagating carbenes gave an alternative strategy to design new monomers which could be polymerized via more stable propagating carbenes. Generally, Ru-alkylidenes are reported to undergo decomposition through the formation of bimolecular complexes.[34,44,45] In particular, recent work by the Lee group demonstrated that alkyne-chelated Ru−alkylidene complexes are stabilized by *gem*-dimethyl groups at the propargyl carbon.[46] To investigate how this dimethyl group could affect the stability of the propagating carbene during CP, we prepared a new
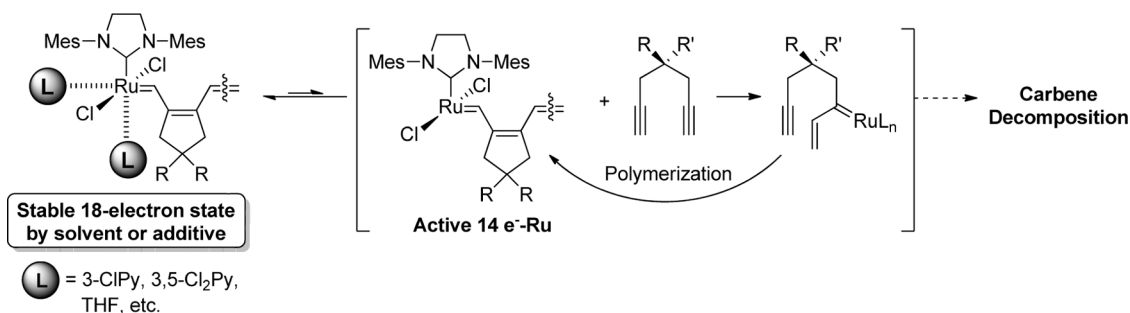
Figure 8. Proposed scheme to show the effects of weakly coordinating ligands.

monomer, **M1-a**, an analog of **M1**, and performed the same kinetic analysis in DCM-d_2 at room temperature (Figure 9).
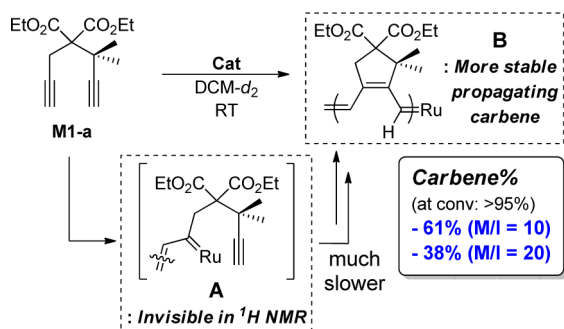

Figure 9. ^{1}H NMR measurements of the propagating carbene during polymerization of **M1-a**.

This polymerization proceeded much more slowly than for **M1**, especially initially, because both ring closing and propagation were significantly retarded by the *gem*-dimethyl substituent (Figure 9 and Figures S2 and S3). Although benzylidene efficiently underwent the initiation by reacting with the sterically less demanding terminal alkyne, it was difficult to monitor the carbene concentration during the initial stages of propagation because the disubstituted carbene intermediate **A** (Figure 9) (without any proton was invisible in ^{1}H NMR and was the major species at the initial stage because of the much slower ring-closure.

With increasing conversion, the carbene peak (corresponding to the actual propagating species **B**, Figure 9) grew, and the carbene% was monitored by ^{1}H NMR. The remaining carbene % was measured after 95% monomer conversion and was found to be 61% (M/I = 10, after 3 h) and 38% (M/I = 20, after 5 h). As expected, these values were higher than the corresponding carbene% of **M1** in the previous kinetic analysis (Figure 5, 43% for M/I = 10 and 13% for M/I = 20). This result suggests that the sterically hindered dimethyl group near the propagating carbene provided some shielding effect or protection, thereby increasing the carbene lifetime.

Finally, we conducted the CP of **M1-a** with M/I = 50 at room temperature in DCM; even without the additive, full conversion was achieved, although it required a much longer reaction time (10 h) because of much slower cyclization and propagation owing to the 3,3-dimethyl group. This again showed that higher conversion of **M1-a** (compared to **M1**; Table 1, entry 1) was possible because of greater stabilization of the propagating carbene (Figure 10). Moreover, PDI value of the polymer produced at room temperature was quite narrow (1.38), suggesting that chain transfer is also suppressed by the
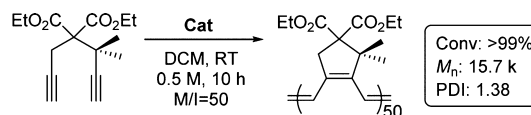

Figure 10. Cyclopolymerization of **M1-a** in DCM at room temperature.

steric effects of dimethyl substitution (compared to a PDI of 2.56; Table 1, entry 1). With a lower M/I=25, the polymer having M_n of 7.9 kDa and PDI of 1.13 was obtained after 7 h. These experiments provide significant insights into CP, as the polymerization efficiency could be predicted from quantitative carbene analysis. We expect that this strategy will be helpful in investigating other CP systems.

■ CONCLUSION

In summary, we demonstrated successful CP of 1,6-heptadiyne derivatives in DCM using the third-generation Grubbs catalyst and 3,5-Cl$_2$Py. Various monomers were successfully polymerized through living polymerization to afford polymers with excellent molecular weight control and narrow PDIs. Mechanistic studies using ^{1}H NMR revealed that weakly coordinating reagents (THF and 3,5-Cl$_2$Py) suppressed the decomposition of the propagating carbene (a 14-electron state) and increased the turnover numbers of the reactions. Kinetic analyses of the reaction order showed that living polymerization was possible in the presence of weakly coordinating reagents at lower temperatures, because the propagating carbenes were stabilized and chain transfer was suppressed. Consequently, block copolymer with molecular weight higher than those shown in the previous report was successfully produced. As an alternative strategy to stabilizing the propagating carbene, we introduced *gem*-dimethyl substituents into the 3-position on the 1,6-heptadiyne derivative. This steric protection effectively increased the carbene lifetime of the new monomer, improving the turnover number. In brief, an improved understanding of the mechanistic details of CP in DCM allowed for the targeted modification of the reaction conditions, which significantly enhanced the monomer scope and utility of the reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, characterizations, SEC traces, kinetic data, and NMR data for new compounds and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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