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Bidentate Phenoxides as Ideal Activating Ligands for Living Ring-Opening Alkyne Metathesis Polymerization

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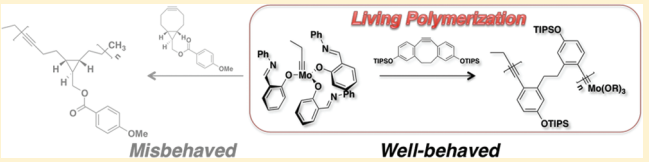
Supporting Information

ABSTRACT: We describe here a well-behaved initiator for ring-opening alkyne metathesis polymerization (ROAMP) of dibenzocyclooctynes. The reaction produces living polymers with low polydispersities and predictable molecular weights. We activate the well-known alkyne metathesis precatalyst, $[(N(t\text{Bu})Ar)_3Mo{\equiv}CCH_2CH_3]$, with phenolic ligands that have σ-electron donating substituents. We show that the chelating ability of these ligands as well as the nature of the propagating molybdenum center have dramatic effects on the outcome of the polymerization reaction.



We herein report the use of bidentate, chelating phenoxides as activating ligands for an exceptionally well-behaved ring-opening alkyne metathesis polymerization (ROAMP) initiator. The active molybdenum alkylidyne complex is formed in situ through a fast ligand exchange reaction of the bulky amide ligands in $[(N(t\text{Bu})Ar)_3Mo{\equiv}CCH_2CH_3]$[1] (**1**) with three equivalents of a phenol additive.[2] These initiators are similar to well-known Mo and W alkyne metathesis catalysts.[1c,d,3] Chelating substituents (in complexes **2** and **3**) in combination with a ring-strained dibenzocyclooctyne monomer **4**[4] at low temperatures give polymers with low polydispersities and highly predictable molecular weights. The structure of the ring strained alkyne and the resulting structure of the reactive intermediate molybdenum species strongly influence the course of the polymerization: while dibenzocyclooctynes yield very well-behaved polymerization reactions, aliphatic substrate **5**[5] yield polymers whose PDIs and M_ns indicate a less disciplined reaction sequence.

Efficient initiators for the ring-opening metathesis polymerization (ROMP) of strained alkynes, cousin to the widely used olefin ROMP, have until recently remained elusive, and only a few examples have been disclosed.[6] We previously reported the first example of living ROAMP yielding polymers with exceptionally narrow molecular weight distributions. The reaction gave poly((1,2-diphenylethane)-2′,2″-ethynylene) from dibenzocyclooctyne **6** using the Mo alkylidyne complex **2**.[7] These results led us to speculate that the superior performance of the ROAMP initiator in the presence of **2** is due at least in part to its ability to reversibly chelate to Mo via the oxygen atoms of the *o*-nitro group.[8,9] While this system gives polymers featuring very low PDIs, the molecular weights of the resultant chains were approximately an order of magnitude higher than would be expected from the monomer/initiator loading. The combination of near-unity PDIs and excessively high molecular weights suggests that only a fraction of the added Mo alkylidyne initiated and contributed to the polymer chain growth. In this study, we explore a new phenolic ligand system derived from *N*-phenyl salicylimine (**3**, see Figure 1) and its potential to control the propagation step of the ROAMP by reversible chelation to the molybdenum.[9]

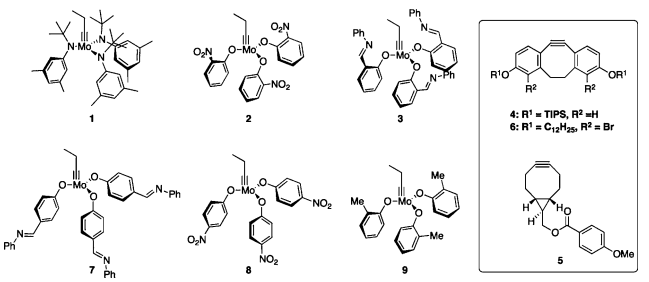


Figure 1. Structures of molybdenum alkylidyne complexes (**1**, **2**, **3**, **7**, **8**, and **9**) and monomers (**4**, **5**, and **6**).

In a standard polymerization experiment the activated complex (1 equiv of **1**, 3 equiv of phenol ligand, toluene, 5 min, 24 °C)[10] is added directly via syringe to 5 mol equiv of monomer **4** in toluene at −78 °C. To monitor the progress of the reaction aliquots are taken from the reaction mixture at regular intervals and are quenched with methanol to yield **poly-4** (Scheme 1). ^{1}H NMR experiments indicate that all monomer is consumed within less than 30 s from the addition of the activated initiator (Figure S3, Supporting Information). GPC analysis of quenched aliquots from the polymerization reaction shows no variation in either the identities or the distributions of

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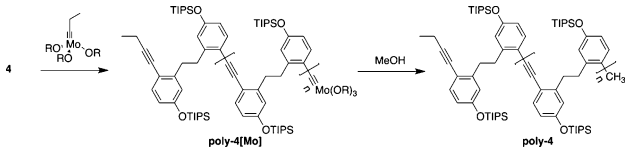
Scheme 1. Polymerization of 4 with Molybdenum-Based Initiators



the reaction products subsequent to the initial formation of polymer.[11,12] The GPC traces for the polymerization of **4** at −78 °C with five different initiators (**2**−**3**, **7**−**9**) are depicted in Figure 2A. We find that that **2** and **3** give polymers of adequate

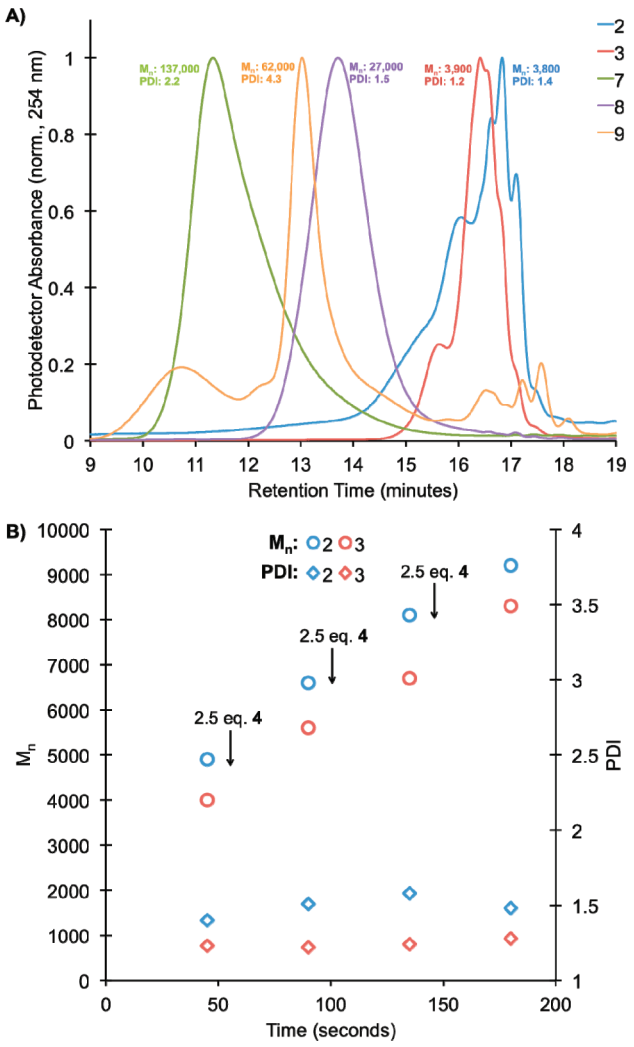


Figure 2. (A) GPC data of polymerizations of **4**; sample quenched after t = 15 s. Reaction conditions: −78 °C; **4**:**1**:**ArOH** = 5:1:3. (B) GPC of aliquots taken at 45, 90, 135, and 180 s from a living polymerization. 2.5 equiv of monomer were added at 60, 105, and 150 s.

molecular weight (M_n ~ 4000) for a 5:1 loading of monomer to initiator, and that these polymers have low polydispersity (PDI = 1.4 for **2** and 1.2 for **3**). Mass spectrometric analysis of a polymer sample formed in the presence of **3** is consistent with the formation of oligomers ranging from the trimer to the nonamer and terminated at either end with a butynyl and a methyl group (Figure S9, Supporting Information). We made a few attempts to increase the monomer loading in polymerizations with **3**, but this did not prove to be straightforward due to the solubility properties of the higher molecular weight polymers. Ongoing research is dedicated to overcoming these limitations. The multimodality of the lower molecular weight polymers is likely due to the resolution of the GPC columns.

The well-behaved reactions of initiators **2** and **3** are in stark contrast to those performed with control compounds, i.e., compounds whose ligands cannot bind in a chelating mode to the molybdenum. In complexes **7** and **8**, the nitro or imine substituents are in the para-position; complex **9** has a methyl group in the ortho position. All three of these complexes yield degrees of polymerization that are 1−2 orders of magnitude greater than expected for the monomer/initiator loading, indicating an exceptionally fast propagation once the polymerization is initiated. Consequently, less than 10% of the metal centers contribute to the formation of polymer chains. We hypothesize that ligands with ortho substituents that can reversibly coordinate the molybdenum in a bidentate mode slow the rate of propagation of the ring-opening metathesis polymerization.[9] The chelating ligand stabilizes the intermediate propagating molybdenum alkylidyne complex, and thus provides sufficient time for all molybdenum centers to initiate before the monomer is consumed. The small difference in reactivity observed for complexes **2** and **3** can be attributed to the more efficient stabilization of the propagating molybdenum species by the σ-donating lone pair of the imine N atom as opposed to the O atoms of the nitro group.

We tested these new initiators for evidence that they initiate a living polymerization. If the active molybdenum complex remains attached to one end of the growing polymer chain during the propagation phase a linear increase in molecular weight should be observed and should not be accompanied by any increase in polydispersity. With an initial loading of 5:1 monomer:intitator, a ROAMP reaction was allowed to proceed for 45 s.[13] An aliquot was quenched and then 2.5 equiv of **4** was added to the original polymerization mixture. A second aliquot was taken from the mixture after a delay of 30 s. This cycle of addition/delay/aliquot removal was repeated a third and fourth time, and all four polymers were analyzed by GPC. The GPC data obtained for these polymerizations is summarized in Figure 2. Iterative addition of 2.5 equiv of monomer to the reaction mixture leads to a linear increase in molecular weight while the PDI remains essentially unchanged. We conclude that the propagating molybdenum species at one end of the growing polymer chain is not deactivated when all the monomer in the reaction mixture is consumed. The unchanged PDI is further evidence that sequentially added monomer is readily incorporated into growing polymer chains rather than initiating a new polymerization. On the basis of these experiments we infer that the molybdenum complexes featuring bidentate activating ligands (**2** and **3**) support well-behaved living polymerizations.

The ROAMP of **4** initiated by **2** changes dramatically if it is performed at room temperature. The PDI of the resulting polymers is ~1.3, but the average molecular weight is 1 order of magnitude higher than expected based on the initial monomer/initiator loading. When we use **3** at room temperature, we again observe a low molecular weight material with a narrow weight distribution (PDI ~ 1.2). Polymerizations performed at 25 °C using **7**, **8**, and **9** again yield only high molecular weight polymers (PDI > 3.0). We attribute the difference in reactivity between **2** and **3** to the greater σ-donating ability of the imine substituent. Since the PDIs of the polymers yielded by **2** and **3**

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are so similar yet the M_ns are so different, we conclude that essentially all of the Mo sites are active in the case of **3**, but only 10−15% of the sites are active in the case of **2**. GPC data for **4** are gvien in Figure 3.

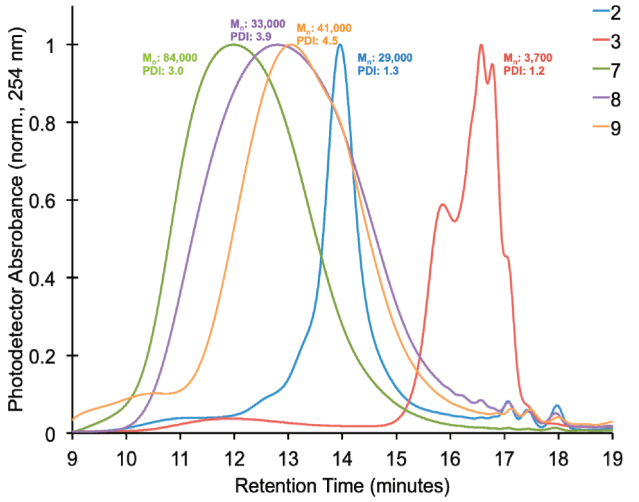
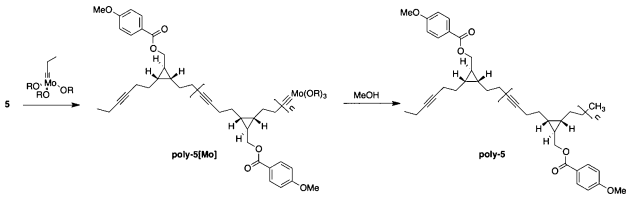


Figure 3. GPC data of polymerizations of **4**; sample quenched after t = 15 s. Reaction conditions: 24 °C; **4**:**1**:**ArOH** = 5:1:3.

Mechanistic considerations based on Katz alkylidyne/metallacyclobutadiene[14] intermediates indicate that the ROAMP of dibenzocyclooctyne monomer **4** should proceed via a benzylidyne intermediate (**poly-4**[**Mo**]). Since the initial Mo complex is an aliphatic alkylidyne (Scheme 1), we sought to investigate a process that retains the aliphatic substituent throughout the reaction. In order to evaluate the substrate effect on the ROAMP with chelating ligands, we synthesized **5** as an easily accessible solubilized model system (Scheme 2).[15]

Scheme 2. Polymerization of 5 with Molybdenum Initiators



As we observed in the polymerization of **4**, all monomer **5** is consumed in less than 15 s at −78 °C (Figure S8, Supporting Information). We found that these conditions yield polymers with higher than expected M_n (M_n from 6000−10000; expected M_n ∼ 1500) and PDIs ranging from 1.4−1.8, noticeably higher than for **4** under the same conditions. Furthermore, these polymerizations were not found to be living (Figure S11, Supporting Information). Figure 4 shows the GPC traces of the polymerizations of **5** after 15 and 120 s. Unlike in the cases of the dibenzocyclooctynes, these polymers continue to evolve over time, with the notable exception of those made using complex **3**.[16] A significant decrease in M_n was observed for initiators **2** and **9**, which can presumably be attributed to cross metathesis. An increase in M_n was observed for initiators **7** and **8**. As shown in Figure 4, PDI's varied by initiator. Because we observe no clear trend among the different initiator systems, we conclude that the ability of bidentate ligands to control

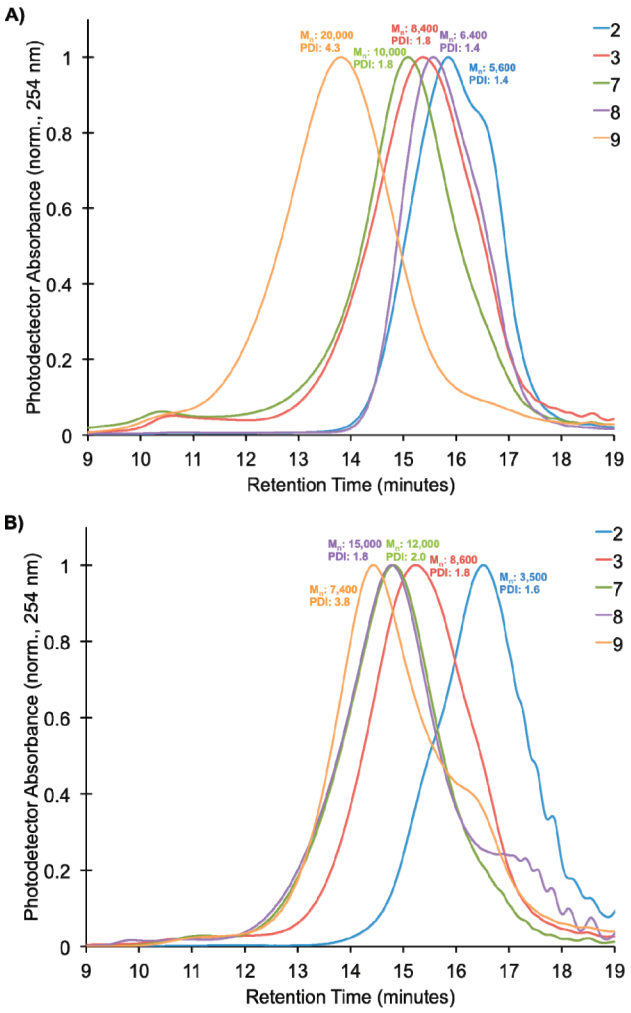


Figure 4. GPC data of polymerizations of **5**; Reaction conditions: −78 °C; **5**:**1**:**phenol** = 5:1:3. (A) Sample quenched after t = 15 s. (B) Sample quenched after t = 120 s.

ROAMP depends heavily on the nature of the propagating molybdenum species.

Table 1 summarizes the results for the ROAMP of monomers **4** and **5** at −78 °C with the molybdenum alkylidyne complexes **2**, **3**, **7**, **8**, and **9**. Dramatic difference in the ROAMP reaction of dibenzocyclooctynes can be observed when *ortho*-substituted phenoxide ligands are used: (1) molybdenum alkylidyne complexes featuring chelating phenoxide ligands (**2**, **3**) react more slowly with dibenzocyclooctyne monomers than

Table 1. M_ns and PDIs after 15 s of Polymers Synthesized Using Initiators 2, 3, 7, and 8

no.	mono.	init.	T, °C	M_n	PDI	living?
1	**4**	**2**	−78	3800	1.4	yes
2	**4**	**3**	−78	3900	1.2	yes
3	**4**	**7**	−78	27 000	1.5	no
4	**4**	**8**	−78	137 000	2.2	no
5	**4**	**9**	−78	62 000	4.3	no
6	**5**	**2**	−78	5600	1.4	no
7	**5**	**3**	−78	8400	1.8	no
8	**5**	**7**	−78	6400	1.4	no
9	**5**	**8**	−78	10 000	1.8	no
10	**4**	**9**	−78	20 000	4.3	no

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the monodentate controls (**7**–**9**). (2) Upon reaction of the $Mo(OAr)_3$ propylidyne initiator with the first monomer – the initiation step in the polymerization sequence – a benzylidyne is generated in the case of the dibenzocyclooctyne monomer **4**, while another alkylidyne is generated in the case of aliphatic cyclooctyne **5**.

When bidentate phenoxides are used as activating ligands in the polymerization of dibenzocyclooctyne **4**, the initiation step is faster than the chain propagation. All molybdenum propylidynes added to the monomer mixture can initiate a polymer chain before the monomer is consumed by the ensuing propagation phase. It should be noted that only phenoxides with chelating ortho-substituents have this effect. In the case of nonchelating phenoxide ligands both the initiation step and the propagation step proceed at similar rates. The structure of the resulting polymers is dictated by the few molybdenum alkylidynes that initiate and rapidly consume all monomer present in the reaction mixture. We expected to observe the same trend in the polymerization of the aliphatic ring-strained monomers. The observation that a small difference in the structure of the propagating species—a molybdenum alkylidyne complex in **poly-5**[**Mo**] or a molybdenum benzylidyne in **poly-4**[**Mo**]—significantly changes the performance of the ROAMP initiator lets us conclude that along with the natures of the ligands and monomer, the overall complex structure of the propagating molybdenum–alkylidyne/benzylidyne bond is of paramount importance.

This study demonstrates that bidentate ligands and the nature of the strained monomer have a dramatic effect on the characteristics of ROAMP of strained cyclic alkynes. It also provides vital insight into the design requirements of initiators for ROAMP. These initiators will be useful for generating new polymers and precursors to nanostructured forms of carbon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, synthesis diagrams, characterization data and spectra for **3**–**5**, **7**, **poly-4**, and **poly-5**, and GPC analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

GPC, gel permeation chromatography; M_n, number-averaged molecular weight; PDI, polydispersity index; ROAMP, ring-opening alkyne metathesis polymerization; ROMP, ring-opening metathesis polymerization

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(5) Synthesis and characterization of **5** can be found in the Supporting Information. The synthesis is derived from: Dommerholt, J.; Schmidt, S.; Temming, R.; Hendriks, L. J. A.; Rutjes, F. P. J. T.; van Hest, J. C. M.; Lefeber, D. J.; Friedl, P.; van Delft, F. L. *Angew. Chem.* **2010**, *122*, 9612–9615; *Angew. Chem., Int. Ed.* **2010**, *49*, 9422–9425.

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(9) For an early example on the use of reversibly binding ligands to control propagation rate with respect to initiation rate, see: Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146–151. For a review on living olefin ROMP, see: Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1–29.

(10) Initiator activation conditions were chosen to follow the Moore protocol, which utilizes three phenolic ligands per equivalent of [Mo].^{1}H NMR experiments indicate that the ligand exchange of the amides on **1** with phenols is fast. There is evidence that multiple molybdenum complexes with different degrees of substitution are present in solution (see Figures S1 and S2, Supporting Information).

(11) See Supporting Information, Figures S3–S6, for time-resolved GPC analysis of polymerization of **4** with each initiator at −78 °C.

(12) The M_n and PDI of the resulting polymers were determined via GPC and are calibrated to polystyrene standards.

(13) We note that there is a difference in the observed M_n of polymers initiated by **2** that are collected after 45 s and those collected after 15 s. We attribute this to the less robust initiation of **2** when compared with **3**. This is consistent with the higher PDI's observed for **2** at both room temperature and −78 °C.

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(15) A 4-methoxybenzoyl group increases the solubility and provides a UV chromophore for GPC analysis.
(16) See Figures S12−S15, Supporting Information for for time-resolved GPC analysis of polymerization of **5** with each initiator at −78 °C.