

Ring Opening Metathesis Polymerization of Cyclic Allenes

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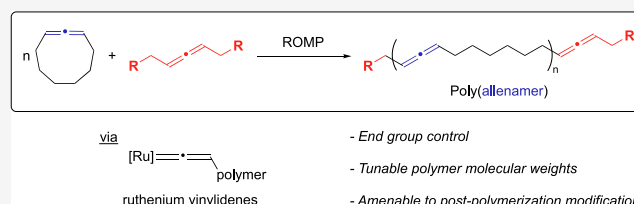
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ABSTRACT: The ring opening metathesis polymerization of cyclic allenes is described. Treating the monomers to a Grubbs-type catalyst afforded polymers that featured allenes integrated into their main chains, as confirmed through a range of spectroscopic, chromatographic, and chemical techniques. Acyclic, 1,3-disubstituted allenes were used as chain transfer agents in the aforementioned reactions. These additives not only provided the corresponding end-functionalized polymers but also enabled control over the molecular weights of the polymers produced. The polymers obtained from the ring opening metathesis polymerization reactions were transformed into silyl-containing derivatives using a hydrosilylation-based, post-polymerization modification. A polymerization mechanism was also deduced and proposed to proceed through a process that involved ruthenium vinylidene intermediates and selective chain transfer.



INTRODUCTION

The allene is a unique functional group that features a sp -hybridized carbon atom flanked by two sp^2 -hybridized carbon atoms.¹ The π -orbitals which comprise the cumulated double-bonds are orthogonal, which effectively prevents electronic delocalization across the system and enables the allene to react as an isolated alkene.² However, due to its unique geometry coupled with a relatively high s orbital contribution and a high degree of unsaturation, allenes are typically more reactive than alkenes and thus have attracted attention for use in a wide range of synthetic transformations,³ including cycloadditions,^{4–6} regioselective heteroatom additions,^{7–10} and enantioselective reactions.^{11–14} Allenes have also found significant utility in macromolecular chemistry.^{15–44} Similar to vinylic monomers, such as ethylene, propylene, or styrene, addition polymers are formed by subjecting allenes to various types of radical,^{20,45,46} cationic,^{21,24} or transition metal-based^{23,27,29,31,43} catalysts and, depending on the polymerization mechanism, 1,2- and/or 2,3-regioisomers can form as possible products (see Scheme 1). Such polymers are unsaturated and relatively carbon-rich⁴⁷ and thus are amenable for further modification or adaptation. Moreover, allene addition polymerization methodologies have matured such that derivatives outfitted with aryl,²⁹ alcohol,³⁵ ester,³⁶ amide,³² and other functional groups may be readily polymerized. Recently, it was demonstrated that different structural classes of allenes can be copolymerized to obtain polymeric materials with tunable properties.^{30,43}

Polymers that feature allenyl groups embedded in their backbones are relatively rare.^{47,48} To the best of our knowledge, the first example of such a polymer was reported by Ochiai (1999).⁴⁹ Approximately 10% of the repeat units found in poly(4-phenyl-1-buten-3-yne), which was obtained via an anionic polymerization, feature allenyl units. Kijima later

(2002) demonstrated that a nickel-catalyzed dehalogenative polycondensation of 1,3-bis(4-bromophenyl)-1,3-diphenylpropadiene afforded a polymer with an alternating combination of allenyl and biphenylene repeat units.⁵⁰ More recently (2020), Brantley showed how the polymer obtained from the ring-opening metathesis polymerization (ROMP) of norbornene may be transformed into allenyl-containing derivatives using the Doering–Moore–Skattebøl reaction.⁵¹

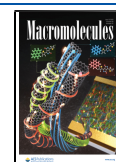
We hypothesized that polymers with allenes in their main chains, noted herein as “poly(allenamer)s”, may be obtained via the ROMP of cyclic allenes. ROMP is a reaction where the release of the ring-strain associated with the monomer drives the formation of polymers.⁵² While the methodology is commonly used to polymerize strained cyclic alkenes (e.g., *cis,cis*-1,5-cyclooctadiene or norbornene),^{53–66} other unsaturated hydrocarbons, such as cyclic alkynes, have also been utilized.^{67–70} A unique feature of ROMP reaction is that the functional groups present in the cyclic monomers employed are retained in the metathetical polymers produced. Moreover, the use of allenes in metathesis chemistry is precedented. For example, mono-substituted acyclic allenes have been converted into 1,3-disubstituted derivatives via cross metathesis³⁴ and α,ω -bisallenes have been ring-closed to afford cyclic allenes.⁷¹

Very recently, Neary and Moore disclosed a validation of the aforementioned hypothesis.⁷² They reported that the ROMP of 1,2-cyclononadiene using the Grubbs second generation catalyst

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Scheme 1. (Top) General Allene Addition Polymerization Reaction and (Bottom) Examples of Methods that Have Been Used to Synthesize Poly(allenamer)s

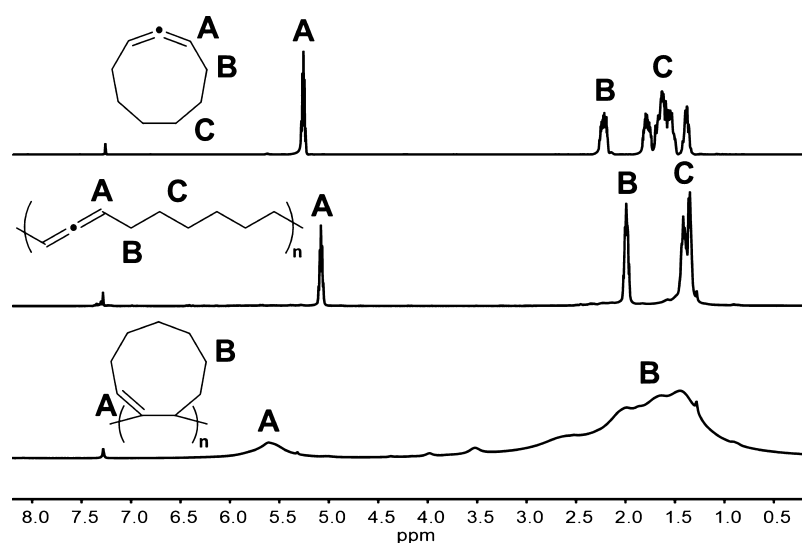
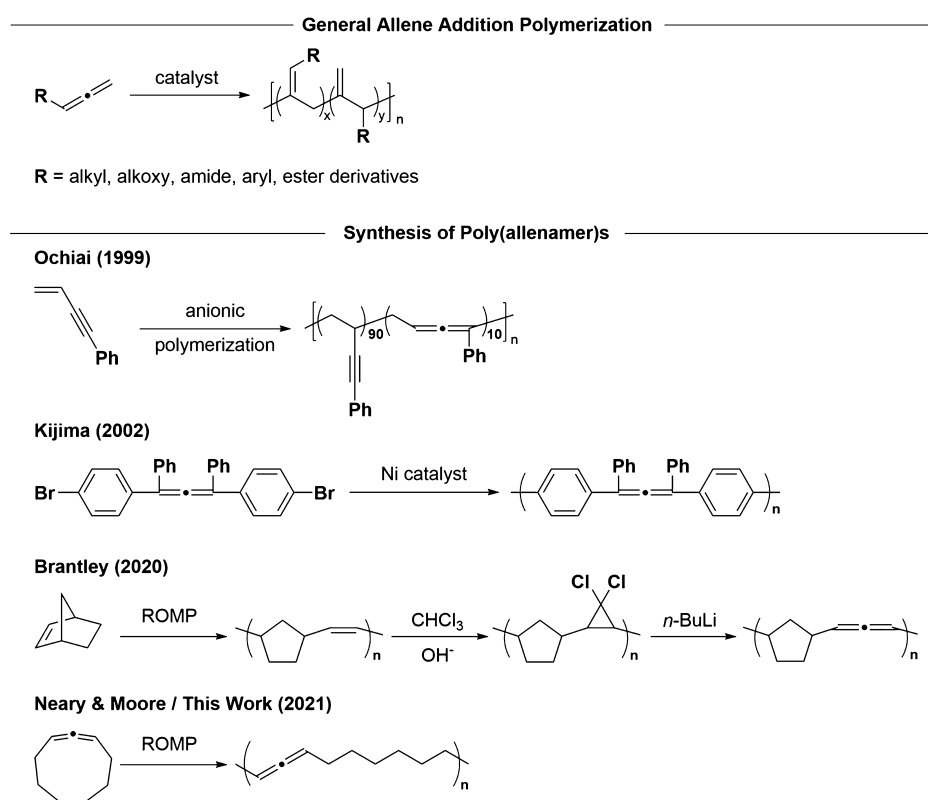


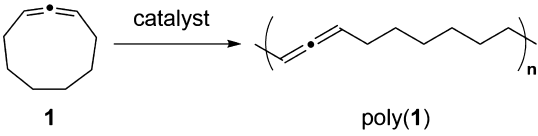
Figure 1. ^1H NMR spectra recorded for **1** (top), poly(**1**) (middle), and the addition polymer of **1** (bottom) (CDCl_3 , 25°C).

(**G2**) affords a poly(allenamer). The kinetics of the reaction were also investigated, and the underlying polymerization mechanism was elucidated to proceed through Ru alkylidene intermediates. Prompted by the disclosure, a summary of our results is provided here. We will show that subjecting 1,2-cyclononadiene and other cyclic allenes to the Grubbs third generation catalyst (**G3**) also affords poly(allenamer)s but that the reaction may proceed via a distinct mechanistic pathway. We also demonstrate that the addition of allenyl-based chain transfer agents (CTAs) in the aforementioned ROMP reactions offers a means to obtain end-functionalized polymers with tailored end-

groups and tunable molecular weights.^{73–79} Finally, we will show that the chemical potential of the poly(allenamer)s may be harnessed through post-polymerization modifications. The results described below are complementary to the previous report and aim to enrich our understanding of using allenes in metathesis-based polymer chemistry.

RESULTS AND DISCUSSION

In an initial experiment, a tetrahydrofuran (THF) solution of 1,2-cyclononadiene (**1**)^{80–83} ($[\mathbf{1}]_0 = 2.0\text{ M}$) was treated with **G3** (1 mol %) at room temperature. The color of the reaction

Table 1. Summary of Polymerization Conditions and Results^a


entry	catalyst	solvent	$[M]_0/[I]_0$	$[M]_0$	T (°C)	$M_{n, \text{theo}}^b$ (kDa)	$M_{n, \text{exp}}^c$ (kDa)	\bar{D}	yield (conversion) (%) ^d
1	G3	THF	100	2.0	25	4.3	7.0	1.6	33 (35)
2	G3	toluene	100	2.0	25				0 (trace)
3	G3	CH ₂ Cl ₂	100	2.0	25	3.7	3.0	1.8	25 (30)
4	G3	<i>n</i> -hexane	100	2.0	25				0 (trace)
5	G3	chlorobenzene	100	2.0	25				0 (trace)
6	Mo	THF	100	2.0	25				0 (0)
7	G1	THF	100	2.0	25				0 (0)
8	G2	THF	100	2.0	25	4.2	8.9	2.0	20 (34)
9	HG2	THF	100	2.0	25	4.5	8.6	2.1	25 (37)
10	G3	THF	100	2.0	-25				0 (0)
11	G3	THF	100	2.0	0	1.3	8.0	2.1	10 (11)
12	G3	THF	100	2.0	60	7.3	10.2	2.0	55 (60)
13	G2	THF	100	2.0	60	8.6	10.4	2.9 ^e	63 (70)
14	HG2	THF	100	2.0	60	7.7	11.2	2.6 ^e	46 (63)
15	G3	1,4-dioxane	100	2.0	80	5.1	10.1	2.5	30 (42)
16	G3	1,4-dioxane	100	2.0	100	7.1	12.4	2.5	50 (58)
17	G3	THF	50	2.0	60	5.1	7.0	2.6	75 (83)
18	G3	THF	25	1.0 ^f	60	3.1	6.2	2.0	90 (99)
19	G3	THF	25	0.1	60	3.1	1.0	1.6	92 (99)
20	G3	THF	25	6.7 ^g	60				0 (trace)

^aConditions: $[1]_0 = 2.0$ M, 30 min. ^bTheoretical number average molecular weight ($M_{n, \text{theo}}$) = molecular weight of **1** $\times [M]_0/[I]_0 \times$ % conversion. ^cExperimental number average molecular weight ($M_{n, \text{exp}}$) was determined by SEC in THF against polystyrene standards. ^dDetermined by ¹H NMR analysis of an aliquot that was removed from the reaction mixture. ^eBroad, bimodal distribution. ^fThe reaction mixture became gelatinous when $[1]_0 = 1.5$ M, although the FT-IR spectrum of the insoluble product was similar to the result recorded for poly(**1**) (see Figure S5). ^g $[1]_0 = 6.7$ M (neat).

mixture gradually changed from green to dark brown. After 30 min, excess ethyl vinyl ether was added to quench the polymerization reaction and the resulting mixture was poured into excess methanol. Assuming the structure shown for poly(**1**) and quantitative initiation, the yield of the reaction was determined to be 35% and the material was predicted to have a number average molecular weight (M_n) of 4.3 kDa. The polystyrene-equivalent number M_n of the polymer and its polydispersity index (\bar{D}) were measured to be 7.0 kDa and 1.6, respectively, using size exclusion chromatography (SEC). The difference between the theoretical and experimental molecular weights coupled with the relative broad polydispersity was attributed to chain transfer (*vide infra*).

A range of spectroscopic and chromatographic techniques were used to analyze poly(**1**). For comparison, the addition polymer of **1** was also prepared³⁰ and analyzed. As shown in Figure 1, distinct differences were observed upon inspecting the ¹H NMR spectra that were recorded for the two polymers. Poly(**1**) exhibited a sharp resonance at 5.04 ppm (CDCl₃), which was assigned to the allenyl protons in the polymer backbone. For comparison, the monomer displayed a similar signal, albeit it was slightly upfield (5.26 ppm), whereas the addition polymer exhibited a broad signal in the region typically expected for protons attached to alkenyl moieties (5.57 ppm). Diagnostic signals were also observed at 204 ppm and 1960 cm⁻¹ in the ¹³C NMR and FT-IR spectra, respectively, recorded for poly(**1**) (see Figure S1); these signals were not observed in the corresponding spectra recorded for the addition polymer or

the monomer. Based on these results, we concluded that the structure of poly(**1**) was consistent with that shown.

Subsequent efforts were directed toward optimizing the ROMP chemistry; key results are summarized in Table 1. Unless otherwise noted, the initial monomer concentration ($[1]_0 = 2.0$ M), the monomer-to-initiator feed ratio ($[M]_0/[I]_0 = 100$), and the polymerization temperature (25 °C) were kept constant in each of the following experiments. First, a range of solvents was explored, including CH₂Cl₂, toluene, *n*-hexane, and chlorobenzene; and optimal results were obtained in THF presumably due to the relatively high stability of the catalyst in this solvent (see Figure S2).^{72,84} The use of 2,6-diisopropylphenylimidoneophylidene molybdenum(VI) bis(hexafluoro-*t*-butoxide) (i.e., Schrock's Catalyst, **Mo**) or the Grubbs first generation catalyst (**G1**) in lieu of **G3** did not result in any observable reaction upon exposure to **1** as determined by NMR spectroscopy. In contrast, the Grubbs second generation catalyst (**G2**) as well as the Hoveyda–Grubbs second generation catalyst (**HG2**) afforded conversions of monomer to polymer similar to **G3** (~35%).

Since ROMP reactions are enthalpically driven by the release of ring-strain and entropically disfavored, it was hypothesized that lower reaction temperatures would increase the yield of polymers. However, no reaction was observed when the reaction was conducted at -25 °C and only a 11% conversion of monomer to polymer was measured at 0 °C. Although elevating the reaction temperature to 60 °C increased monomer conversion to 60%, significant improvements were not observed when higher temperatures (80 or 100 °C in 1,4-dioxane) were used. By analyzing a series of stoichiometric mixtures of **1** and **G3**, it was determined that catalyst initiation efficiency also

Scheme 2. Synthesis of poly(1) in the Presence of Various Chain Transfer Agents (2–4)

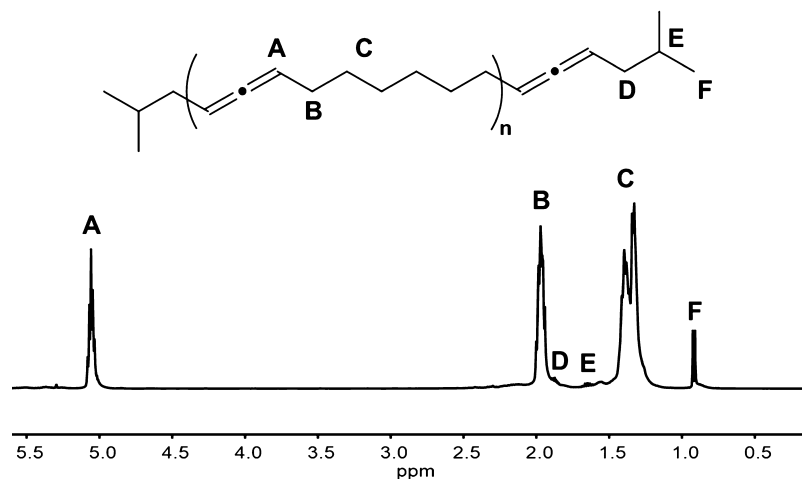
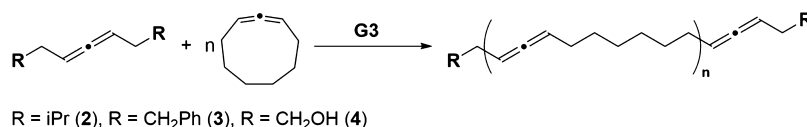


Figure 2. ¹H NMR spectrum recorded for an end-functionalized polymer that was prepared via the ROMP of **1** in the presence of CTA **2** (CDCl₃, 25 °C).

improves with temperature (see Figure S3). Since relatively optimal results were obtained at 60 °C, the polymerization reactions were separately repeated using **G2** as well as **HG2** in lieu of **G3** as the initiator. Although comparable conversions were observed, the polymers obtained using the former featured bimodal molecular weight distributions, whereas **G3** yielded unimodal polymers (see Figure S4). The molecular weights of the polymers produced appeared to depend on monomer conversions, although the initial monomer-to-initiator ratio as well as the initial monomer concentration were found to be contributing factors as well. In general, the use of a higher [1]₀/[G3]₀ ratio or a lower [1]₀ afforded higher yields of lower molecular weight polymers. Polymerization was not observed in neat monomer, presumably due to premature catalyst decomposition.⁸⁵

As part of an effort aimed at improving control over the molecular weight of the polymers produced, the inclusion of CTAs in the reaction mixtures was considered.^{52,86} The ROMP of cyclic alkenes in the presence of α,ω -disubstituted acyclic alkenes, which effectively function as CTAs, has been shown to be an effective method for not only controlling polymer molecular weight but for producing end-functionalized polymers.⁷⁵ When chain transfer is efficient, the polymerization approximates a step-growth polymerization and the molecular weight of the polymer produced approaches the monomer-to-CTA feed ratio. To ascertain if a similar approach could be used to control the ROMP of cyclic allenes, 2,8-dimethylnona-4,5-diene (**2**), an allene outfitted with isobutyl groups, was synthesized according to literature procedures^{87,88} and explored as a CTA.

As shown in Scheme 2, a THF mixture **1** and **2** (10 : 1 molar ratio; [1]₀ = 2.0 M) was treated with **G3** (2 mol %) and then stirred at 60 °C for 30 min. Afterward, the polymerization reaction was quenched by the addition of excess ethyl vinyl ether and the resulting mixture was poured into excess methanol. The precipitate that formed was collected via filtration and washed

with methanol to remove any residual starting material. As shown in Figure 2, ¹H NMR analysis of the isolated material revealed that the structure of the polymer was similar to that of poly(**1**); however, new signals were observed at 1.88 ppm (m, H^d), 1.65 ppm (septet, H^e), and 0.92 ppm (d, H^f), which were assigned to the isobutyl end-groups. Integration of the end-groups followed by comparison to the repeat unit indicated that the M_n of the polymer was 6.6 kDa. For comparison, the polymer was measured to have a M_n of 5.0 kDa by SEC. As summarized in Table 2 and Figure S6, repeating the aforementioned experi-

Table 2. ROMP of **1** in the Presence of CTA **2**^a

entry	[1] ₀ /[2] ₀	[1] ₀ /[G3] ₀	M _n ^b (kDa)	<i>D</i>	yield (%)
1	100	50	9.9	2.5	71
2	50	50	7.3	2.8	92
3	20	50	6.9	2.8	92
4	10	50	4.7	2.2	99
5	10	100	5.5	2.0	50
6 ^c	10	20	3.8	2.6	96
7 ^c	10	10	2.2	2.1	99

^aConditions: [1]₀ = 2.0 M in THF, 30 min. ^bDetermined by SEC in THF against polystyrene standards. ^cSince gelation was observed when [1]₀ = 2.0 M, the initial monomer concentration was reduced to 1.0 M.

ments with different monomer-to-CTA ratios revealed that the molecular weights of the polymers produced correlated with the feed ratio. Similarly, varying the [1]₀/[G3]₀ while holding the [1]₀/[2]₀ constant was also found to affect the molecular weight of the polymer produced and provided further support for chain transfer. Allenes **3** and **4**, which feature pendant and hydroxyl functional groups, respectively, were also synthesized and utilized as CTAs.^{88,89} For example, the ROMP of **1** in the presence of CTA **3** or **4** (10:1 molar ratio; [1]₀ = 2.0 M; 2 mol % **G3** for **3** and 1 mol % **G3** for **4**) afforded poly(**1**) with the expected phenethyl or hydroxyethyl end-groups. The M_n values,

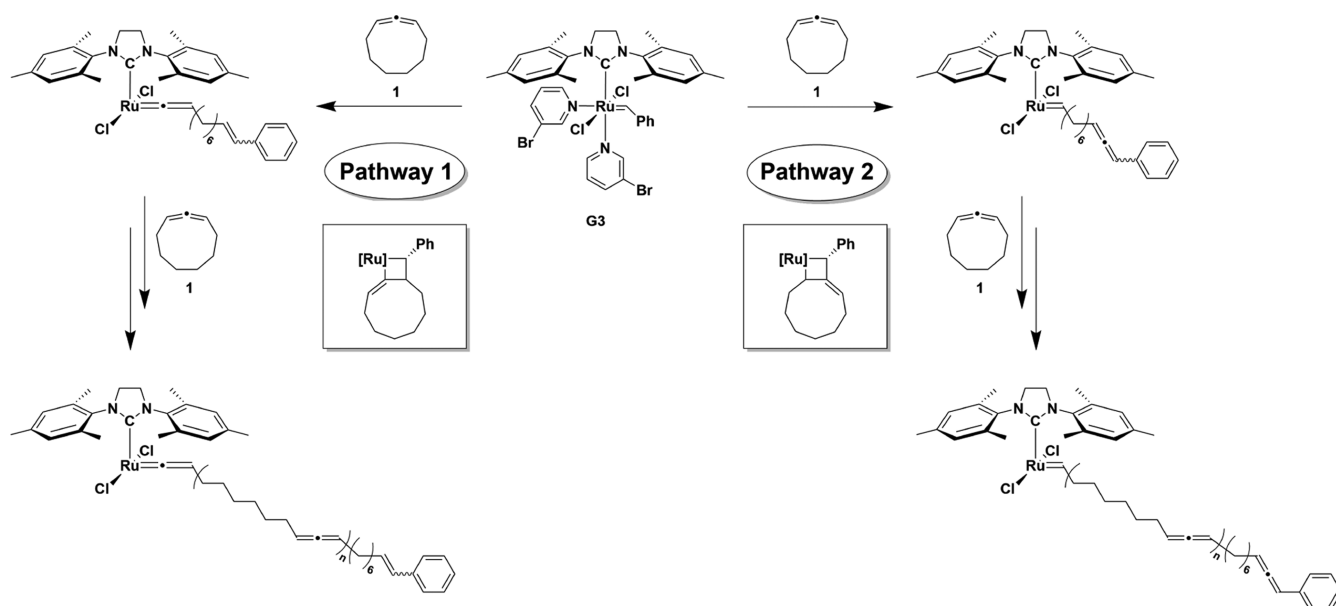


Figure 3. Proposed mechanistic pathways.

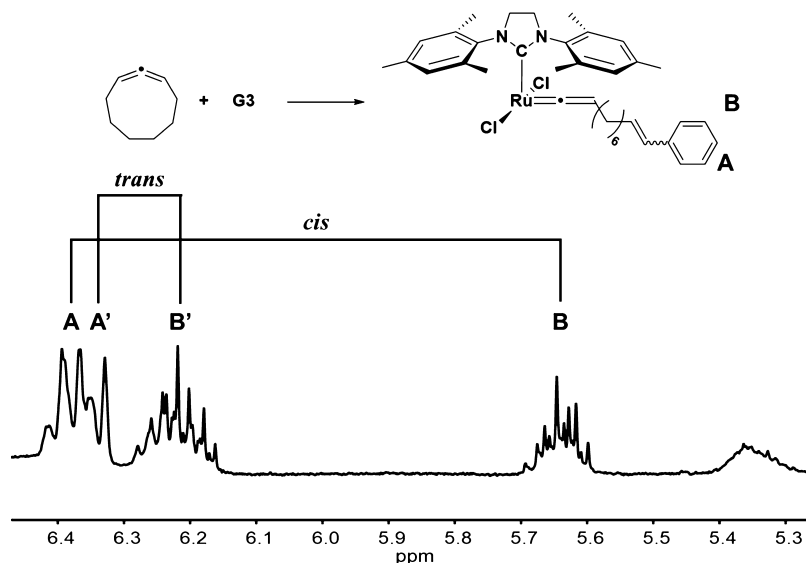


Figure 4. Partial ^1H NMR spectrum recorded for an equimolar mixture of **1** and **G3** (CDCl_3 , 60°C).⁹⁹

as calculated using ^1H NMR spectroscopy, were also comparable to their SEC-derived values (c.f., 4.5 kDa vs 4.2 kDa and 8.9 kDa vs 7.2 kDa, respectively).

As described in Figure 3, two possible mechanistic pathways can be envisioned and depend on monomer insertion vis-à-vis the formation of ruthenium alkylidene or vinylidene intermediates. The mechanism appeared to be selective as polymers with [3]cumulene^{90,91} or alkene repeat units were not observed in any of the experiments described above. To distinguish between the two potential pathways shown, each of which affords the observed poly(allenamer)s, efforts were directed toward the identification of the propagating catalytically active species. A CDCl_3 solution of **1** ($[\mathbf{1}]_0 = 20\text{ mM}$) was treated with an equimolar quantity of **G3** for 5 min at 60°C and then analyzed by ^1H NMR spectroscopy. Downfield signals were observed over the range of 5.66 to 6.40 ppm and assigned to terminal *cis* ($\sim 33\%$) and *trans* ($\sim 66\%$) styrenyl moieties (Figure 4).^{92,93} Moreover, the distinctive Ru benzylidene ^1H

NMR signal of **G3** (19.1 ppm) transformed into a new, broad signal at 5.35 ppm, which was attributed to the formation of a Ru vinylidene.^{94,95} Additional support for vinylidene formation was obtained when a CDCl_3 solution of **G3** ($[\mathbf{G3}]_0 = 360\text{ mM}$) was treated with 5 molar equivalents of **1** at 60°C and then analyzed by ^{13}C NMR spectroscopy, which resulted in the identification of a new, diagnostic signal at 350 ppm (see Figure S8).^{96–98} Initiation as well as monomer conversion were quantitative. Collectively, these observations were consistent, indicating that the polymerization mechanism predominately proceeds through Pathway 1. Neary and Moore reported that the ROMP of **1** using **G2** proceeds through Ru alkylidene intermediates and thus the polymerization mechanism may be sensitive to the catalyst structure and/or the conditions employed.

Since allenes have been used in a broad range of chemical transformations, the potential of transforming poly(**1**) into allylsilyl or vinylsilyl derivatives via a post-polymerization hydrosilylation was explored. Unsaturated silanes are versatile

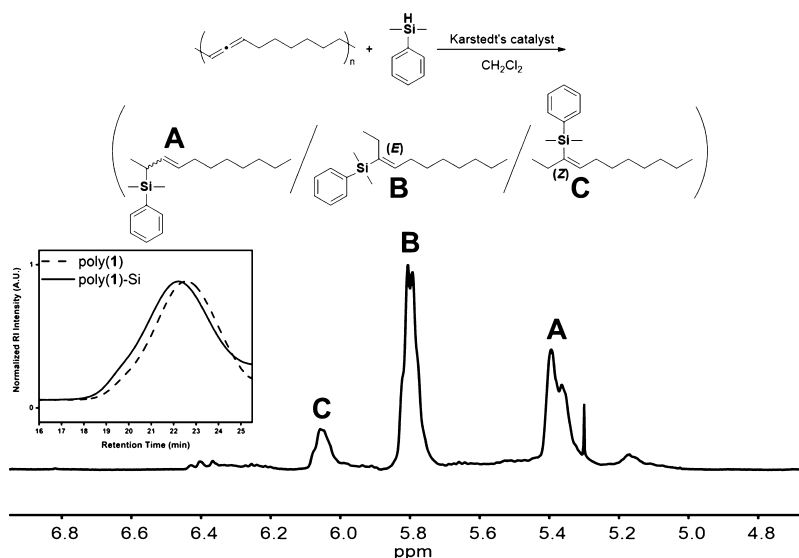
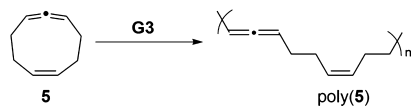


Figure 5. (Top) Hydrosilylation of poly(1) and (bottom) corresponding ^1H NMR spectrum recorded for the hydrosilylated product (poly(1)-Si) (CDCl_3 , $25\text{ }^\circ\text{C}$). Inset: SEC data collected for poly(1) and poly(1)-Si (indicated).

reagents for use in cross-coupling reactions^{10,100–104} and polymers that feature such groups have been converted into various types of functional derivatives.^{105,106} As shown in Figure 5, a CH_2Cl_2 solution of poly(1) ($[\text{I}]_0 = 0.2\text{ M}$) was treated with dimethyl(phenyl)silane (1.9 equiv) and Karstedt's catalyst (5 mol %).^{107,108} After 12 h at room temperature, the reaction mixture was poured into methanol and the resulting precipitate was collected. Analysis of the precipitate revealed that the characteristic ^1H NMR signals of poly(1) disappeared and were replaced with new alkenyl signals, which were assigned to different hydrosilylated isomers: 1,2-addition product (A), 23%; *E*-1,3-addition product (B), 62%; and *Z*-1,3-addition product (C), 15%.^{10,109,110} In addition, SEC showed that the M_n of the hydrosilylated polymer shifted toward a higher value when compared to the starting material (c.f., 6.0 kDa vs 5.3 kDa), which provided further support for the post-polymerization modification.

Finally, efforts were directed toward exploring whether other cyclic allenes could be polymerized using G3. 1,2,6-Cyclo-nonatriene (5) was selected, prepared from *cis,cis*-1,5-cyclo-octadiene (COD) using the Doering–Moore–Skattebøl reaction and subjected to G3 using optimized conditions ($[\text{S}] = 1.0\text{ M}$, THF, 4 mol % G3, $60\text{ }^\circ\text{C}$, 20 h); see Scheme 3. The

Scheme 3. ROMP of 5 Using G3



resulting polymer was obtained in 70% yield based on the presumed structure and determined by SEC to feature M_n of 2.4 kDa ($D = 2.2$). The ^1H NMR spectra recorded for poly(5) featured two signals at 5.09 and 5.41 ppm, which were assigned to the allenyl and the alkenyl groups in the polymer backbone, respectively. Similarly, the alkenyl units exhibited a ^{13}C NMR signal at 129.7 ppm, whereas the allenyl units were observed at 90.7 and 204.0 ppm. Integration of the signals indicated that the two functional groups were present in an equimolar ratio. A signal at 27.2 ppm was also observed in the ^{13}C NMR spectrum

recorded for poly(5), which indicated that the geometry of the alkenes in the polymer backbone were predominately *cis*. Additional support for the assignment was obtained via FT-IR spectroscopy, which revealed that the polymer exhibited a strong absorbance at 727 cm^{-1} .^{111,112}

CONCLUSIONS

The third generation Grubbs catalyst was found to initiate the ROMP of various cyclic allenes and afforded polymers that feature allene functional groups in their backbones. Derivatives comprising alternating allenyl/alkenyl repeat units were also prepared. Adding CTAs to the polymerization reactions afforded end-functionalized polymers and facilitated control over molecular weight. Subjecting the poly(allenamer)s to standard hydrosilylation conditions revealed that the polymers can be transformed using standard post-polymerization modification methodology. When the third generation Grubbs catalyst was used as an initiator, the polymerization mechanism appeared to be selective and involved Ru vinylidene intermediates. Overall, the results are complementary to recent reports and, collectively, can be expected to guide catalyst selection and optimized conditions. In a broader perspective, the ROMP of cyclic allenes facilitates access to an underdeveloped class of unsaturated polymers with high potential for further modification and/or for use in a broad range of contemporary applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.1c00571>.

General considerations; additional synthesis details; ^{13}C NMR spectra recorded for 1, poly(1), and the addition polymer of 1; full/partial FT-IR spectra recorded for 1, poly(1), and the addition polymer of 1; partial ^{13}C NMR spectra recorded for a 5:1 mixture of 1 and G3 in various solvents; partial ^1H NMR spectra recorded for a 1:1 mixture of 1 and G3 (25 and $60\text{ }^\circ\text{C}$); SEC data recorded for poly(1) obtained using G2, HG2, or G3; partial ^1H NMR spectrum recorded for ROMP of 1 under neat

conditions; SEC data recorded for poly(**1**) obtained using varying $[1]_0/[G3]_0$ and $[1]_0/[2]_0$; partial ^1H NMR spectra recorded for poly(**1**); partial ^{13}C NMR spectra recorded for a 5:1 mixture of **1** and **G3**; full ^1H NMR spectrum recorded for a 1:1 mixture of **1** and **G3**; full FT-IR spectra recorded for poly(**5**); and additional NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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