Ring-Opening Metathesis Polymerization of Butyl Substituted *trans*-Cyclooctenes

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ABSTRACT: The synthesis and ring-opening metathesis polymerization of highly-strained 3- and 1-butyl-*trans*-cyclooctenes was investigated with the goal of quickly preparing regioregular polymers with narrow molar mass distributions, which could serve as precursors for high precision short-chain branched polyethylene. 3-butyl-*trans*-cyclooctene was unable to be polymerized in a regioregular manner, however 1-butyl-*trans*-cyclooctene did yield regioregular product, although the dispersities were higher than expected. Investigation by NMR provided evidence that the nature of the propagating alkylidene is likely non-uniform throughout the course of the reaction, leading to the broadened molar mass distribution.

Ring-opening metathesis polymerization (ROMP) of cyclic olefins followed by hydrogenation is a powerful method for the production of high precision model polyolefins; it is a chain-growth polymerization, and the stereo- and regiochemistry of the resulting polymer may be controlled through judicious catalyst choice and monomer design.[1-3] Recently, ROMP of 3-alkyl substituted *cis*-cyclooctenes (*c*COEs) using highly active and functional group tolerant ruthenium-based Grubbs second and third generation catalysts (**G2** and **G3**, respectively) was reported to yield perfectly stereo- and regioregular polyalkenamers which, upon hydrogenation, provided highly regioregular short-chain branched polyethylene (SCB PE).[4,5] This lead to a series of reports regarding the use of various *c*COE monomers with other functional groups in the allylic position for the generation of functionalized regioregular PE,[6-10] and has been extended to include group 6 based monoaryloxide pyrrolide (MAP) catalysts as well.[11]

The driving force behind ROMP is the release of ring strain. Thus, polymerizations of 3-substituted *c*COE monomers are typically performed at high concentrations (~2 mol/L) or in bulk monomer with reaction times from 1 to 20 h in order to ensure high conversion.[12] On the other hand, *trans*-cyclooctene (*t*COE) exhibits significantly higher ring strain than its *cis* isomer (16.7 kcal/mol vs. 7.4 kcal/mol for the unsubstituted monomers),[13] and may be polymerized in a living fashion to high molar masses in minutes using the less active first generation Grubbs catalyst (**G1**) in the presence of excess triphenyl phosphine (PPh$_3$), which serves to reduce the rate of secondary metathesis (k_s) and increase the rate of initiation (k_i).[14] Motivated to prepare high molar mass, regioregular polyalkenamers with narrower mass distributions, we explored the ROMP of various butyl-substituted *t*COE monomers, and report the results here. In particular, the goal was to provide a monomer with high ring strain coupled with enough steric bulk to inhibit contributions to the mass distribution from cross metathesis, and thus access narrower mass distributions. We elected to employ butyl as the alkyl group for the studies

performed, as it provides sufficient steric bulk to serve as a model for alkyl chains of varying lengths.

We first explored the ROMP of 3-butyl-*trans*-cyclooctene (**1**) using **G1** in the presence of excess PPh$_3$ in order to provide polymers with narrow molar mass distributions. Monomer **1** was prepared through a three step isomerization[15] beginning with 3-butyl-*cis*-cyclooctene.[16,17] ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy revealed the presence of two species in equal amounts in the product mixture, which correspond to the two possible isomers for monomer **1**.[16] Polymerization of **1** at room temperature with the **G1**/PPh$_3$ system ([M]$_o$ = 0.5 mol/L) at 50 °C lead to the isolation of polymer, with longer reaction times leading to higher yields and number average molar mass (M_n) values closer to the theoretical values based on the initial monomer:catalyst ratio, although the dispersity (Đ) increased with time as well (Table S1).[16] Unfortunately, ^{1}H and ^{13}C NMR spectroscopy revealed that the resulting polymers were highly regio*irregular*, with no preference for *cis* or *trans* geometry about the double bonds in the polymer backbone being observed. Employing *N*-heterocyclic carbene (NHC) ligated **G3** as the catalyst did not lead to any improvement in the regiochemistry of the resulting polymer as judged by ^{1}H NMR.[16] Accordingly, further investigation into the polymerization of **1** was not performed.

Seeking to prevent the possibility of different orientations of the monomer during the [2+2] cycloaddition step, we considered a monomer with the butyl group in the 1 position, which would also prevent the possibility for the presence of multiple isomers. Historically, ROMP of trisubstituted olefins has been challenging, given the large degree of steric bulk at the reactive olefin, often requiring high temperatures, high concentrations, and long reaction times. For example, polymerization of 1-methyl-*trans*-cyclooctene (neat) at 50 °C for 23 h was reported by Katz and coworkers using the well-defined tungsten initiator (Ph)$_2$C=W(CO)$_5$, which produced a regioregular polyalkenamer (within the detection limits of ^{13}C NMR) in 49 % yield. The authors in this work proposed that the regioregularity of the

Scheme 1. Synthesis and ROMP on Monomer 2.

Figure 1. Partial ^{13}C (150 MHz, 25 °C, CDCl$_3$) NMR of poly(1-butyl-*trans*-cyclooctene).
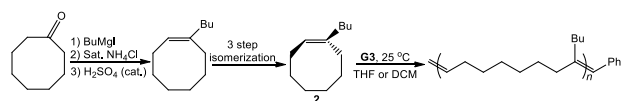
resulting polymer originates from the higher stability of a tertiary propagating tungsten alkylidene, relative to a secondary.[18] It was shown that the same catalyst could effectively polymerize the even more highly strained 1-methylcyclobutene as well, also with a high degree of 'translational invariance'.[19] More recently, it has been reported that 1,5-dimethyl-1,5-cyclooctadiene may be polymerized using various ruthenium based catalysts in a regioregular fashion. However, given the low ring strain and steric bulk of this monomer, long reaction times (24 h) and elevated temperatures (50 °C) and concentrations (2.0 mol/L) were necessary, and polymers with high molar masses (> 30 kDa) have not been disclosed.[20,21] Cyclobutenes bearing a variety of polar functional groups in the 1 position have also been polymerized with a high degree of regioregularity by Sampson and coworkers with functional group tolerant ruthenium catalysts,[22,23] including examples of alternating copolymers.[24]

With knowledge of the behavior of monomer **1** and the reported work regarding ROMP of strained 1-substituted cycloolefins, we sought to expand upon the pioneering work of Katz[18] by exploring the ROMP of 1-butyl-*trans*-cyclooctene (**2**), which was prepared as summarized in Scheme 1.[15,16] Reaction of **2** with **G1**/PPh$_3$ yielded no polymer, even at elevated temperature, likely due to sufficient steric repulsion. The more active catalyst **G3**, on the other hand, which was chosen for its ability to yield polymers with narrow molar mass distributions due to its extremely high k_i value,[25] successfully and quickly polymerized monomer **2** at room temperature in tetrahydrofuran (THF) (Scheme 1), which was chosen as the solvent due to its ability to suppress secondary metathesis.[26] At room temperature, nearly complete conversion (>90% by ^{1}H

NMR) was observed, and high yields were obtained, in very short reaction times (1 m). When larger [M]$_o$:initiator ratios were employed, polymers with M_n values as high as 356 kDa were obtained,[27] and initial monomer concentrations as low as 0.1 mol/L provided high polymer yields.[16] It is likely that the reason the observed M_n values do not track with those expected based on the ratio of monomer to catalyst is due to the fact that the measurements are relative to polystyrene standards; the mean square radius of polystyrene is significantly different than the poly(1-butyl-*trans*-cyclooctene), so a deviation such as this is not unexpected.[27] Polymerizations at low temperatures were also successful, however lower yields were observed, despite the fact that longer reaction times and higher concentrations were employed. Changing solvent to dichloromethane (DCM) also resulted in low yields relative to THF, both at room temperature and below.[16] Unfortunately, Đ values were rather high for all polymerizations, regardless of the conditions employed, the reasons for which are discussed below.

At first glance, NMR spectroscopy suggested that the resulting polymers are perfectly regioregular; the ^{1}H NMR spectrum displays one triplet in the olefin region, while the ^{13}C NMR displays only two olefinic signals (Figure 1). Both *cis* and *trans* isomers likely exist, but the extent of each is difficult to determine. The olefinic resonances observed by both ^{1}H and ^{13}C NMR for these isomers would not be expected to be distinguishable, given the similar magnetic environment caused by the presence of the butyl group on the alkene. However, close inspection of the ^{1}H NMR does show overlapping triplets for the methyl protons on the end of the butyl group, and the ^{13}C NMR spectrum displays more signals in the aliphatic region than would be expected for perfect stereoselectivity,[16] indicating the presence of both *cis* and *trans* stereoisomers. Further investigation into this issue was not deemed necessary, as the presence of multiple stereoisomers would not impact the structure of the product after hydrogenation.

Closer inspection of ^{1}H NMR data for lower molar mass polymers prepared from monomer **2** revealed that the actual

Entry[a]	[M]$_o$:[Ru]$_o$	Theor. M_n (kDa)[b]	M_n (kDa)[c]	Đ[c]	Yield (%)
1	25	4.2	4.8	1.3	95
2	93	15.5	29.6	1.9	90
3	304	50.6	51.3	1.6	79
4	1015	168.8	116.0	1.6	79
5[d]	4021	668.7	356.1	2.0	70

Table 1. Polymerization results for monomer 2. [a]Polymerizations were performed as summarized under anaerobic conditions using G3 as the catalyst, THF as the solvent, reaction time = 1 m, and [M]$_o$ = 1.0 mol/L except where indicated. [b]Defined as (MW of 2) × ([M]$_o$:[Ru]) (assuming 100% conversion). [c]Determined by SEC with THF as the eluent at 25 °C at a flow rate of 1 mL/m, calibrated against polystyrene standards.[16,27] [d][M]$_o$ = 1.5 mol/L, reaction time = 10 m.
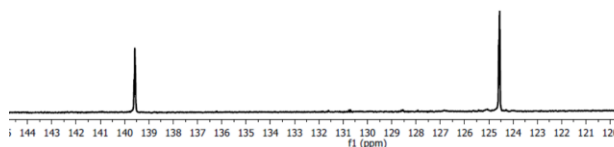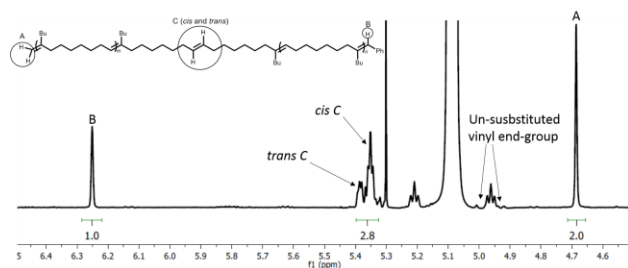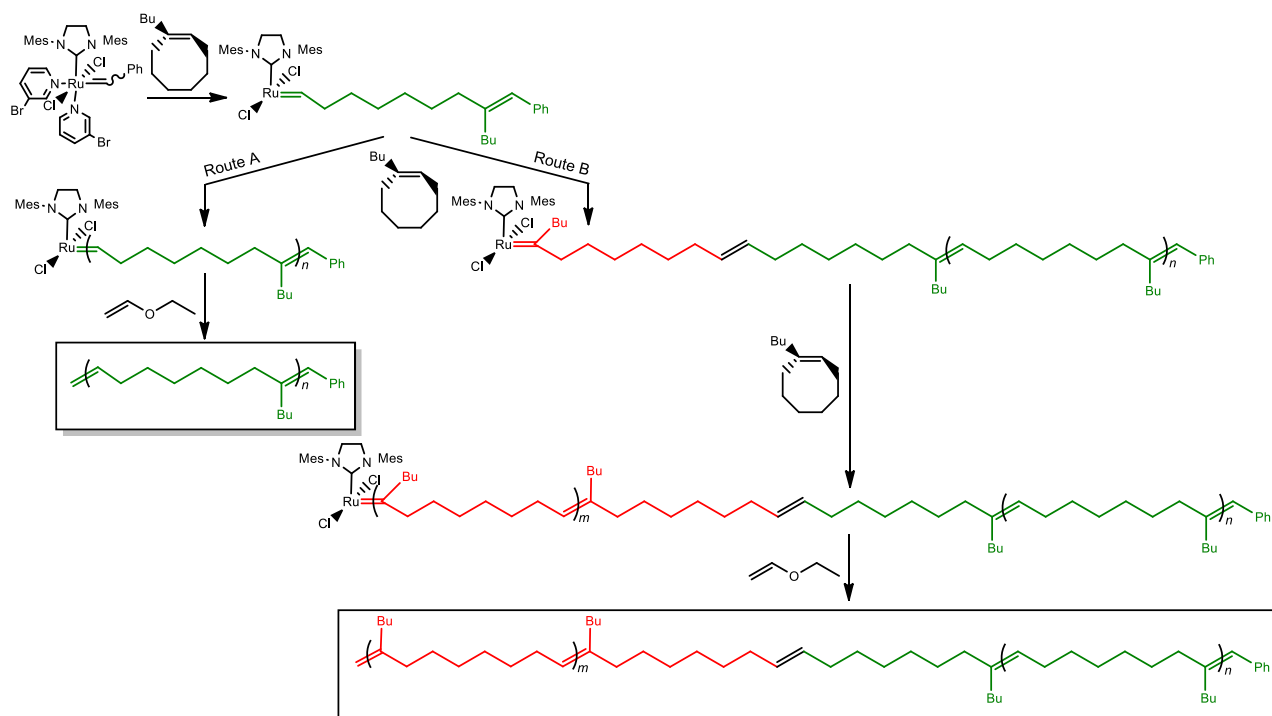

Figure 2. Partial ^{1}H (600 MHz, 25 °C, CDCl$_3$) NMR of poly(1-butyl-*trans*-cyclooctene) of DP = 120. The singlet at 5.30 ppm corresponds to residual DCM.

Scheme 2. Proposed Mechanism of ROMP of Monomer 2 by G3 Leading to 'Flip' in Monomer Orientation.

selectivity in monomer orientation during chain-growth is not as straight forward as originally thought. For example, a polymer with a degree of polymerization (DP) = 120 was prepared according to the procedure in Scheme 1, and the ^{1}H NMR is shown in Figure 2. The singlet at 6.26 ppm indicates that the first monomer exclusively adds with the butyl group distal to the ruthenium center, likely for steric reasons. Two resonances are seen, however, for the vinyl end group of the polymer chain. In minimal concentration, a monosubstituted vinyl group is observed as two small doublets (conclusively identified by comparison against unsubstituted polymers prepared by known procedures[14]) which corresponds to polymerization *via* Route A in Scheme 2. The majority of end groups display one singlet at 4.70 ppm, however, which is indicative of Route B, wherein the orientation of the monomer changes at some point during polymerization. Although the vinylidene protons are indeed chemically distinct, they are indistinguishable by NMR, given the similarity of the butyl group and aliphatic polymer chain, and are observed as one singlet rather than two. Such a 'flip' in monomer addition would result in one unsubstituted olefin linkage in the polymer backbone, which is observed as multiplets seen at 5.41 to 5.34 ppm that match perfectly to the *cis* and *trans* olefin resonances for unsubstituted poly(cyclooctene) (Figure 2).[28] Therefore, overall the polymer is regioregular, however one defect is present, randomly placed along the backbone, as a result of the switch from head-to-tail addition to tail-to-head addition. Evidence for a similar change in monomer orientation may have been observed in the past, but was not explained.[29]

The reason for this observed change in monomer addition is likely electronic in nature. Fomine and coworkers have shown through computations that for NHC ligated ruthenium metathesis catalysts, such as **G3**, the ruthenium center bears non-trivial partial positive charge when bonded to a secondary alkylidene.[30] Therefore, after the first monomer addition, the metal is highly electrophilic and less sterically hindered, making coordination of monomer **2** with the butyl group proximal to ruthenium favorable, as the olefinic carbon which coordinates to ruthenium bears two electron donating alkyl groups. Computations further suggest that although a tertiary alkylidene is sterically unfavorable, this negative interaction is offset by stabilizing electronic factors.[30] Sequential additions after the generation of the tertiary alkylidene will proceed in this same manner in order to minimize unfavorable steric interactions that would result in a tetrasubstituted olefin, which is not observed at all by ^{13}C NMR. This limits the number of misinsertions to a maximum of 1 per chain, resulting in an overall regioregular polymer. The regioregularity observed in ROMP of 1-substituted cyclobutenes arises from monomer addition with the functional group directly on the alkylidene carbon,[22] as well as from the propensity to avoid creating tetrasubstituted olefins, although in the case of carbonyl substituted cyclobutenes the electronics of the monomer are obviously much different. Integration of the unsubstituted olefinic linkage in the polymer backbone integrates slightly greater than the expected 2:1 ratio relative to the styrenic end group, although it appears this may be due to coincidental peak overlap when compared to unsubstituted poly(*trans*-cyclooctene).[14] One may initially assume that the error in regioregularity in the polymer backbone occurs as a result of secondary metathesis rather than monomer misinsertion, however we find this explanation to be unlikely given that i) secondary metathesis typically results in a high molar mass population,[14,31] but these polymers exhibit low molar mass 'tails' by GPC (discussed below), ii) the large degree of steric hindrance at the acyclic backbone olefins would likely inhibit secondary metathesis, iii) minimal change in molar mass and dispersity is observed during a kinetics experiment, as would be expected in the absence secondary metathesis,[16] and most

notably iv) a higher degree of monosubstituted vinyl end group is observed when the monomer:catalyst ratio is decreased to 25, but all other conditions held constant,[16] indicating that the change in orientation occurs due to insertion of monomer, *not* from secondary metathesis, which is equally probable with both low and high monomer:catalyst ratios employed.

As mentioned above, Đ values were consistently higher than one would expect when using **G3**. Specifically, a low molar mass tail was observed in all size exclusion chromatography (SEC) traces.[16] This was attributed to the change in monomer orientation during polymerization, resulting in a change in the nature of the propagating catalyst, from a secondary to a tertiary alkylidene. A tertiary alkylidene would be expected to have a lower k_p value than a secondary alkylidene based simply on sterics, and computations suggest that it would also be less active due to electronic factors.[30] Therefore, when the polymerization begins, all ruthenium species propagate at the same rate. However, over time, the generation of tertiary alkylidenes results in catalysts that propagate more slowly, and the relative population of these species changes over time. The result, therefore, is the presence of a low molar mass tail in the final polymer distribution. This hypothesis is supported by the fact that a low molar mass polymer (*e.g.* Table 1, entry 1) displays a Đ value more in line with those expected for polymers obtained from **G3**. In this case, the low DP of the resulting polymer (25) limits the opportunity for the misinsertion described above, thus limiting the population of catalysts with lower k_p.

Hydrogenation of poly(1-butyl-*trans*-cyclooctene) was performed using *p*-toluenesulfonylhydrazide. Given the steric bulk at the olefins to be hydrogenated, the process had to be repeated several times in order to obtain fully hydrogenated polymer. Near (observably) perfect regioregular short-chain branched polyethylene was observed as the product by both ^{1}H and ^{13}C NMR (Figure 3),[16] further confirming the high degree of regioregularity of the ROMP reaction.
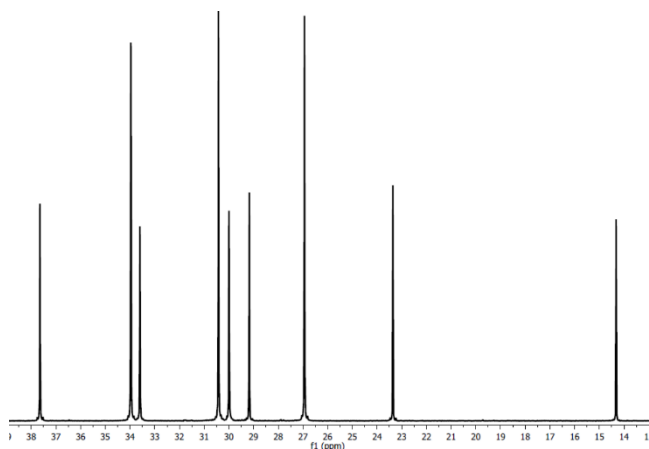

Figure 3. Partial [13]C (150 MHz, 25 °C, CDCl$_3$) NMR of hydrogenated poly(1-butyl-*trans*-cyclooctene).

To summarize, we have investigated the use of ruthenium based ROMP catalysts to prepare regioregular butyl substituted polyalkenamers under mild conditions. Monomer **1** cannot be polymerized in a regioregular manner due to the possibility of the butyl group in the 3 position to orient away from the

supporting ligands, thus allowing for head-to-tail, head-to-head, and tail-to-tail additions. On the other hand, monomer **2** was rapidly polymerized in a regioregular manner by **G3** at room temperature. Unlike previous examples of ROMP of 1-substituted cycloalkenes, in these cases strong evidence exists for a change in the nature of the propagating chain during polymerization, that inserts one defect into the macromolecule, and changes the rate of propagation, resulting in a low molar mass tail and broader dispersity. Given that this misinsertion is highly unlikely to occur more than once throughout the polymerization, and indeed is not observed to do so, its effect on the structure of polymers of higher molar masses is negligible, and the resulting polymers provide highly regioregular short-chain branched polyethylene upon chemical hydrogenation. Unfortunately, the change in propagation rates and distribution-broadening low mass tail will likely only be removed by forcing the first insertion of the monomer into the initiator complex to favor formation of the tertiary ruthenium-alkylidene species.

ASSOCIATED CONTENT

Supporting Information. Experimental details and supporting spectra. 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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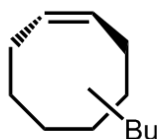
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Highly Strained Alkyl Substituted Cyclic Monomers → [Ru Metathesis Catalyst] → • Short-Chain Branched PE Precursors • High Conversion in Short Reaction Time • High Molar Masses • Low $[M]_o$

Alkyl Position Dictates Regioregularity