The Living ROMP of *trans*-Cyclooctene

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ABSTRACT: The living ring-opening metathesis polymerization (ROMP) of *trans*-cyclooctene (tCO) was investigated. ROMP of tCO in the presence of PPh₃ in THF leads to the formation of narrowly dispersed polycyclooctene (PCO). The presence of PPh₃ as an additive and the use of THF as a solvent were demonstrated to be necessary to suppress competing secondary metathesis processes in the ROMP of tCO. Under optimal conditions, narrowly dispersed PCO was achieved without high molecular weight contaminates. The PCO was then hydrogenated to form linear, narrowly dispersed polyethylene with a melting temperature of 139 °C. Protected, hydroxy-functionalized tCO was polymerized by this method to afford narrowly dispersed, hydroxylated PCO. Block copolymers containing polynorbornene and PCO or containing differentially functionalized PCO were also synthesized and hydrogenated to form block copolymers containing blocks of linear, narrowly dispersed polyethylene.

Ring-opening metathesis polymerization (ROMP) has been employed in the synthesis of a wide range well-defined polymer architectures.[1,2] ROMP is a chain-growth polymerization in which a cyclic olefin is converted to polymer. This process is driven by the release of ring strain which provides the main driving force that is required to overcome the unfavorable entropy change in polymerization.[3] Typical cyclic olefins for ROMP include norbornene, cyclobutene, cyclooctene, and dicyclopentadiene. Also, many functionalized derivatives of these monomers can be polymerized using the functional-group tolerant, late transition metal Grubbs' catalysts **1–3** (Figure 1).[3]

In recent years, living ROMP has emerged as a valuable tool for polymer chemists.[4] A living ROMP polymerization is generally characterized by a low polydispersity index (PDI) < 1.1 and a linear relationship between polymer molecular weight and monomer conversion.[3–5] Norbornene and its functionalized derivatives have become the monomers of choice for living ROMP due to widespread commercial availability, low cost, and general ease of synthesis. Low polydispersity polymers are achieved with living ROMP when the rate of polymer chain initiation (k_i) occurs faster than chain propagation (k_p)[6] and competing secondary metathesis reactions (k_s), including inter- and intramolecular chain transfer by reaction of the initiator with olefins in the polymer backbone, are eliminated. Norbornene exhibits the characteristic high ring strain such needed for irreversible ($k_p \gg k_s$) ROMP (Figure 2) and consequently produces polymers with low PDIs and controllable molecular weights with fast-initiating ($k_i/k_p \geq 1$) catalysts **1** and **3**.[7]

Secondary metathesis is limited by the steric hindrance of the olefins in the backbone of substituted polynorbornenes. In contrast, the living ROMP of monocyclic, unhindered alkenes has seen limited use. Cyclobutene and its functionalized derivatives have been used in living ROMP but to a lesser extent than norbornene.[8–10] Polycyclobutene, with a PDI of 1.1, has been prepared using well-defined tungsten catalysts in the presence of trimethylphosphine (PMe₃).[8] PMe₃, and related trialkyl- and triarylphosphines, have been shown to limit secondary metathesis (*vide infra*). Similarly, Register and co-workers have shown the living ROMP of low strain cyclopentene with well-defined molybdenum alkylidene initiators, also in the presence of PMe₃.[11] Despite the benefits of using a commercially available catalyst and monomer, the low strain of cyclopentene forces the polymerizations to be conducted at
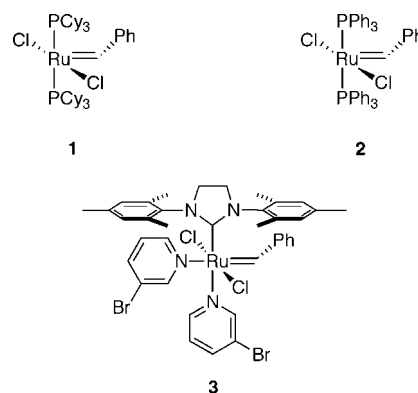

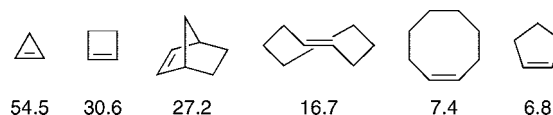**Figure 1.** Ruthenium olefin metathesis catalysts (Cy = cyclohexyl).

| 54.5 | 30.6 | 27.2 | 16.7 | 7.4 | 6.8 |

Figure 2. Relative ring strain for select cyclic olefins (kcal/mol).[12]

high concentration and terminated before full monomer conversion is achieved in order to prevent competing secondary metathesis.

Cyclic *trans*-olefins have been noted as excellent candidates for ROMP because of their high ring strain.[13–15] Nuckolls and co-workers recently reported the living polymerization of *trans,cis*-dibenzo[*a,e*]cyclooctatetrene.[13] Polymers having PDI*s* < 1.1 were formed when the reaction was conducted in the presence of 3 equiv of tricyclohexylphosphine (PCy₃). It was also noted that *cis,cis*-dibenzo[*a,e*]cyclooctatetrene was unreactive under similar conditions. To the best of our knowledge, there are no reports of the living polymerization of *cis*- or *trans*-cyclooctene (tCO) primarily because significant chain transfer from secondary metathesis of the unhindered polymer backbone occurs during ROMP, making it difficult to polymerize in a controlled fashion. *cis*-Cyclooctene has a low ring strain of 7.4 kcal/mol,[12] which lowers its activity for living ROMP. In contrast, tCO has a ring strain of 16.7 kcal/mol (Figure 2).[12] If secondary metathesis can be prevented, highly strained tCO will be excellent candidate for living ROMP polymerization.[16]
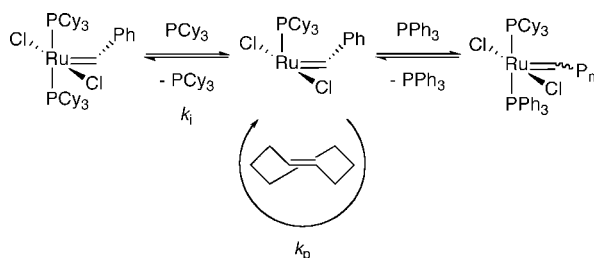
ROMP of *trans*-Cyclooctene. The ROMP of tCO was investigated with several well-known ROMP initiators (Scheme

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Scheme 1. ROMP of *trans*-Cyclooctene
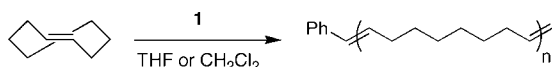
Table 1. Polymerization of tCO in CH_2Cl_2 with $[M]_0/1 = 300$

run	catalyst	$[M]_0{}^a$	M_n ($\times 10^3$ g/mol)^b	% yield^c	PDI
1	**1**	0.50	44	70	1.42
2	**1**	0.05			
3	**2**	0.50	94	77	1.37
4	**2**	0.05	167	69	1.29
5	**3**	0.50	53	64	1.25
6	**3**	0.05			

^{a} Initial Monomer concentration. ^{b} M_n(theo) $= 33 \times 10^3$ g/mol. ^{c} Isolated yields.

Scheme 2. ROMP of tCO with Excess PPh₃

Table 2. Polymerization of tCO with 1 and Increasing PPh₃^a

entry	PPh₃/**1**	$[M]_0/1$	M_n ($\times 10^3$ g/mol)	M_n(theo) ($\times 10^3$ g/mol)	PDI	% yield
1	0	200	39	22	1.30	74
2	1	200	40	22	1.35	74
3	5	200	37	22	1.37	72
4	10	200	32	22	1.31	72
5	20	200	33	22	1.19	67
6	40	200	26	22	1.14	68
7	60	400	55	44	1.06	97
8	0	400	268	44	1.60	76
9	1	400	265	44	1.42	86
10	5	400	213	44	1.31	88
11	10	400	67	44	1.26	93
12	20	400	57	44	1.18	96
13	40	400	46	44	1.13	93
14	60	400	59	44	1.08	90

^{a} Entries 1−7 were conducted in CH_2Cl_2, $[M]_0$=0.5 M at 23 °C; entries 8−14 were conducted under the same conditions, except in THF.
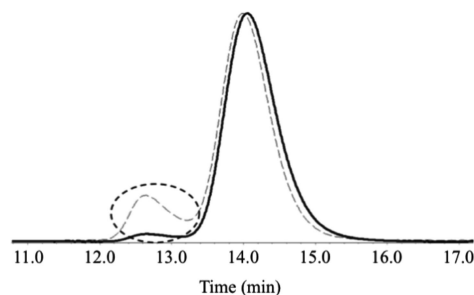

Figure 3. GPC trace of entry 7. RI trace (solid line) and light scattering trace (dashed line). The minor peak (circled) is attributed to competing chain transfer.

1). Table 1 depicts the results of an initial screen of conditions for ROMP of tCO. In runs 1 and 2, catalyst **1** was used to polymerize tCO at high and low concentration, respectively. Run 1 depicts the polymerization of tCO at an initial monomer concentration of 0.5 M in CH_2Cl_2. The observed molecular weight of 44 000 g/mol was higher than the expected value of 33 000 g/mol, and the PDI was 1.42. We noticed that upon the addition of catalyst **1** to a solution of the monomer, the characteristic color change from purple to brown did not occur. Despite complete consumption of the monomer, the lack of color change indicated that the catalyst did not fully initiate and led us to assume that the k_p of tCO is faster than the k_i of **1**. Since all the catalyst did not initiate, the observed molecular weight was higher than the theoretical value based on $[M]_0/1$. The apparently low ratio of k_i/k_p, along with competing secondary metathesis, was inferred to be the cause of the high PDI. When the polymerization was performed at an initial monomer concentration of 0.05 M (run 2), no polymer was formed and only small molecular weight oligomers were observed. Runs 5 and 6 show that when faster initiating catalyst **3** was used, similar results were obtained. Interestingly, polymerization of tCO at 0.05 M using catalyst **2** did yield polymer (run 4). This result was attributed to the much faster k_p and slower k_s of catalyst **2** relative to both catalysts **1** and **3**.[17−19] The observed high molecular weight polymer was the kinetic product resulting from a relatively low k_s/k_p. The broad polydispersity was due to the fact that k_i/k_p for the polymerization of tCO using catalyst **2** was not sufficiently high.

We have previously shown the ROMP of a number of norbornene derivatives as well as cyclooctadiene (COD) using catalyst **1** and excess triphenylphosphine (PPh₃).[20] The resulting polymers had low PDIs and could be prepared with a variety of functionalities. It has been postulated that the excess phosphine competes with monomer for the Ru center, which in turn decreases both the k_p and k_s and possibly generates a bisphosphine catalyst which will only polymerize strained olefins.[20,21] We therefore decided to add excess PPh₃ to the polymerization of tCO using catalyst **1**, as shown in Scheme 2. By increasing the phosphine to catalyst ratio, the concentration

of active catalyst is kept low, similar to a controlled free radical polymerization.[22] Entries 1−7 in Table 2 depict our efforts to reduce secondary metathesis in the polymerization of tCO by varying equivalents of PPh₃ relative to catalyst. As the ratio of phosphine to initiator was increased, the observed polymer molecular weights decreased toward the theoretical values based on $[M]_0/1$, and the PDIs decreased. However, even as the equivalents of PPh₃ were increased, a high molecular weight peak was still observed, as shown in the GPC trace of entry 7 in Figure 3. The refractive index trace (solid line) showed that a small amount of high molecular weight polymer is present and is more pronounced in the light scattering trace (dashed line) because light scattering is dependent on molecular weight while the refractive index is not. Similar high molecular weight species have also been observed in the ROMP of cyclobutene and cyclopentene, respectively.[8,11] Register later demonstrated that acyclic/secondary metathesis competes with ROMP in forming the observed high molecular weight polymers.[23]

In order to further limit the formation of the high molecular weight species, we decided to investigate additional methods of preventing secondary metathesis. It has been demonstrated that as the monomer concentration in solution decreases, the k_p decreases and k_s increases.[20] Thus a decrease in concentration often results in increased PDIs or, in our case, the observed high molecular weight peak. Several reports have suggested that changing the reaction solvent to a more coordinating solvent, such as THF, can limit or even prevent secondary metathesis.[20,24−26] For example, THF has been used to slow the polymerization of cyclooctatetraene and also limit secondary metathesis.[27] We have previously observed that catalyst **1** initiates faster and is less prone to secondary metathesis in solvents such as THF.[20,24] Furthermore, when polymerizations are conducted with early transition metal metathesis catalysts and excess phosphine in THF, secondary metathesis is also suppressed.[8] More recently, Register and co-workers were able to show that the addition of a small amount
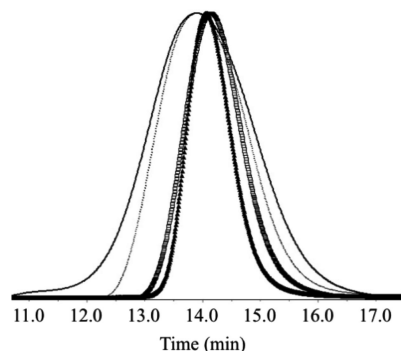
Figure 4. ROMP of tCO with **1** in THF, $[M]_0 = 0.5$ M, at 23 °C with increasing equivalents of PPh$_3$: 0 equiv of PPh$_3$ (solid line), 10 equiv of PPh$_3$ (dotted line), 20 equiv of PPh$_3$ (squares), 60 equiv of of PPh$_3$ (triangles). No high molecular weight peak is observed when >5 equiv of PPh$_3$ relative to **1** are added.

Table 3. Effect of Increasing $[M]_0/1$[b]

entry	$[M]_0/1$	M_n ($\times 10^3$ g/mol)	M_n(theo) ($\times 10^3$ g/mol)	PDI
15	194	31	21	1.10
16	303	42	33	1.08
17	402	48	44	1.08
18	592	66	65	1.09
19[a]	3842	390	429	1.08

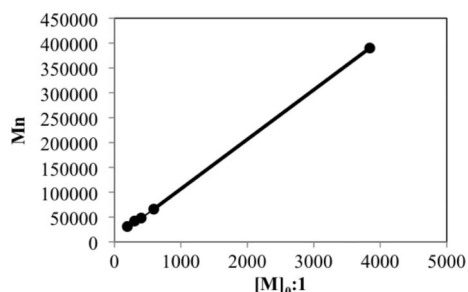[a] $[M]_0 = 0.05$ M. [b] Polymerizations conducted $[M]_0 = 0.5$ M with PPh$_3$/**1** = 60, 23 °C.

Figure 5. Molecular weight control by varying $[M]_0/1$. ROMP of tCO with **1**, $[M]_0 = 0.5$ M with PPh$_3$/**1** = 60 at 23 °C for entries 15−18 in Table 3. The high molecular weight point corresponding to entry 19 was conducted at 0.05 M.

THF limited the secondary metathesis in the ROMP of cyclopentene.[28] After careful examination of these previous reports, we tested the polymerization of tCO in THF with catalyst **1**. Similar to the trend observed in CH$_2$Cl$_2$, decreasing PDIs with increasing phosphine were observed in THF. Interestingly, upon increasing the number of equivalents of PPh$_3$ relative to catalyst beyond five no high molecular weight species was observed, as shown in Figure 4 and Table 2, indicating that chain transfer reactions were subdued. Furthermore, as the ratio of PPh$_3$ to **1** was increased, the observed molecular weight approached the theoretical value based on $[M]_0/1$. These data demonstrate that PPh$_3$ has a greater effect on the k_s than on the k_p of the polymerization.

For a typical living polymerization, molecular weight increases linearly with increasing initial monomer to catalyst ratio ($[M]_0/1$). The results, depicted in Table 3 and Figure 5, clearly show a linear relationship as demonstrated up to molecular weight of 390 000 g/mol and indicate that under the optimized conditions living ROMP of tCO has been achieved.

Reaction Time Study. In order to determine when secondary metathesis was occurring during the course of the reaction, a time study using catalyst **1** was performed (shown in Table 4 and Figure 6). Three samples in either THF or CH$_2$Cl$_2$ were polymerized and terminated at varying times. After a 1-min

Table 4. Time Study[b]

solvent	time (min)	M_n ($\times 10^3$ g/mol)[a]	PDI	% yield
CH$_2$Cl$_2$	1	39	1.10	66
	5	52	1.05	98
	10	52	1.08	99
THF	1	55	1.08	90
	5	52	1.08	90
	10	54	1.08	87

[a] M_n(theo)$=44 \times 10^3$ g/mol. [b] Polymerization conducted with $[M]_0/1 = 400/1$, with PPh$_3$/**1** = 60 at 23 °C.
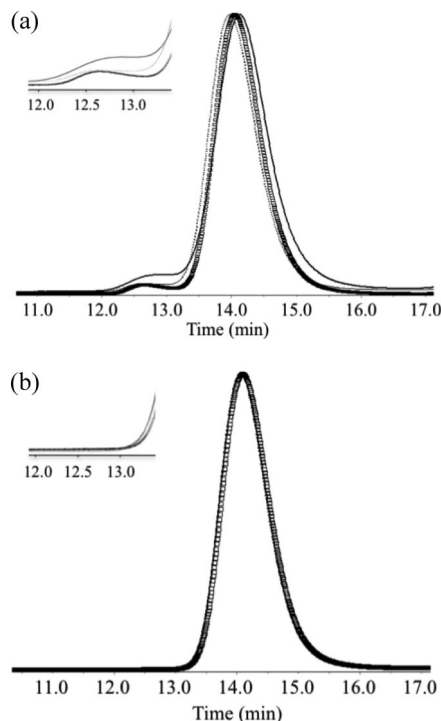
(a)

(b)

Figure 6. GPC traces of polymerizations stopped at increasing times: 1 min (solid lines), 5 min (squares) and 10 min (dotted line). Key: (a) ROMP of tCO in CH$_2$Cl$_2$, $[M]_0=0.5$ M, PPh$_3$/**1**=60, at 23 °C; (b) same as part a except in THF. The reactions were stopped at varying time intervals with ethyl vinyl ether.

reaction time in CH$_2$Cl$_2$, the undesired minor high molecular weight peak was observed and the reaction was not yet complete, as was evident by the presence of unreacted monomer. After 5- and 10-min reaction times in CH$_2$Cl$_2$, the minor high molecular weight peak was still observed. The appearance of a minor high molecular weight peak before complete consumption of the monomer in the 1-min reaction indicates that, under these reaction conditions, secondary metathesis was competing with chain propagation. However, in THF the reaction was complete after 1 min and no minor high molecular weight peak was observed. Furthermore, after 10 min, the polydispersity did not broaden and no high molecular weight species appeared, indicating a living polymerization and no competing chain transfer reactions. These results also point toward a polymerization of tCO in which $k_p \gg k_s$ in THF.

Concentration Study. The limitation in forming monodispersed polycyclooctene using *cis*-cyclooctene is its high critical monomer concentration $[M]_c$.[29] Hocker and co-workers showed that no polymers are formed until the monomer concentration of *cis*-cyclooctene exceeds 0.21 M.[30] As a result, it has been difficult to synthesize ultra high molecular weight PCO (M_n >100 000 g/mol) from *cis*-cyclooctene because the polymerization gels or becomes too viscous when high molecular weight PCO is formed at high concentration. If the initial monomer concentration is less than $[M]_c$, only low molecular weight cyclic

Table 5. Concentration Study[b]

| solvent	$[M]_0$	M_n ($\times 10^3$ g/mol)[a]	PDI	% yield
CH$_2$Cl$_2$	0.25	54	1.08	95
	0.10	56	1.06	35
	0.05	54	1.08	42
THF	0.25	67	1.15	95
	0.10	64	1.10	80
	0.05	64	1.16	81

[a] M_n(theo) = 44 × 10³ g/mol. [b] Polymerization conducted with $[M]_0$/**1** = 400, PPh$_3$/**1** = 60 at 23 °C and for 10 min.

and linear oligomers are formed. Furthermore, it has been shown that critical monomer concentration is directly related to monomer ring strain.[3,29]

tCO has a ring strain of 16 kcal/mol, and, consequently, given the appropriate selection of catalyst and reaction conditions to prevent secondary metathesis, polymerization should occur at more dilute concentrations similar to other highly strained ROMP monomers. In order to test this hypothesis, ROMP of tCO was conducted at concentrations well below the critical monomer concentration of *cis*-cyclooctene, as shown in Table 3, entry 19. Table 5 presents the result of decreasing concentration when polymerizations were performed in either THF or CH$_2$Cl$_2$. When the initial monomer concentration was decreased in CH$_2$Cl$_2$, the molecular weight stayed consistent, but isolated yields were low. The low yields were attributed to an increase in k_s at low concentration and high monomer conversion, which, in turn, formed low molecular weight polymers and oligomers. Low PDIs, and consequently the low isolated yields, were obtained by the removal of these small molecular weight contaminates by fractionation in MeOH. When these same polymerizations were conducted in THF, backbiting was suppressed and high isolated yields were obtained, along with molecular weights consistent with the theoretical value based on $[M]_0$/**1**.

Synthesis of Linear High Density Polyethylene. Linear, monodispersed, high-density polyethylene has previously been synthesized from the ROMP of monocyclic alkenes followed by hydrogenation. Commercially available *cis*-cyclooctene as well as cyclooctadiene (COD) are both well-known monomers for ROMP, and both have been polymerized to form polyethylene, via hydrogenation of polycyclooctene and polybutadiene.[1,2] HDPE without branching can be synthesized from the ROMP of *cis*-cyclooctene or COD followed by hydrogenation, however, the PDIs are high because of secondary metathesis.[3] Acyclic diene metathesis polymerization (ADMET) of dialkene hydrocarbons followed by hydrogenation has also been used to synthesize perfectly linear HDPE. Because ADMET is a step-growth process, the PDIs of the resulting HDPE are around 2.[31] Linear, narrowly dispersed HDPE has previously been synthesized from polycyclobutene and shown to have a T_m of 129 °C; however, cyclobutene is gaseous at room temperature and technical challenges preclude its widespread use. Register and co-workers have shown the synthesis of HDPE from the hydrogenation of polycyclopentene but polymerizations must be conducted at high concentrations and the resulting polymers have high molecular weight contaminants as a result of chain transfer processes.[11] An alternative approach to narrowly dispersed PCO would be the living ROMP of tCO without the high molecular weight contaminates seen previously in the ROMP of cyclopentene. Hydrogenation of the PCO would form linear narrow dispersed HDPE.

Linear PCO, synthesized using catalyst **1** according to the optimal conditions using THF and PPh$_3$, contained 56% *cis* olefin and exhibited a T_m of 10 °C, which is in good agreement with published experimental values.[32,33] Hydrogenation of PCO (Entry 18) was conducted by treatment of the polymer with tosyl hydrazide and tripropyl amine in xylenes[9,34−38] and yielded linear, narrowly dispersed HDPE. The T_m determined for HDPE

Scheme 3. Block Copolymers of Norbornene and tCO[a]
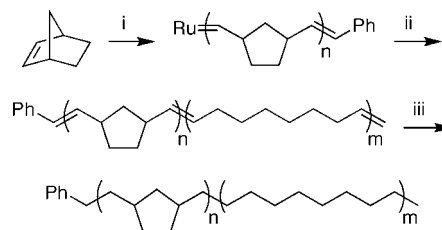
[a] (i) $[M]_0$/**1** = 100, PPh$_3$/**1** = 2, 23 °C, 30 min; (ii) added to a solution of tCO in THF $[M]_0$ = 0.1 M, PPh$_3$/**1** = 58, 23 °C, 10 min; (iii) tosyl hydrazide, ^{n}Pr$_3$N, xylenes 150 °C.
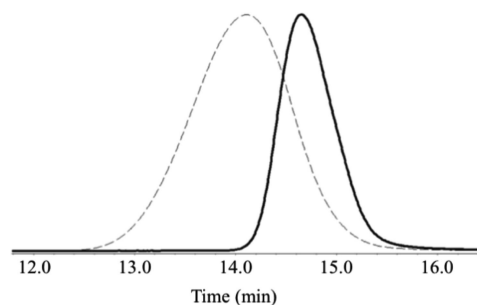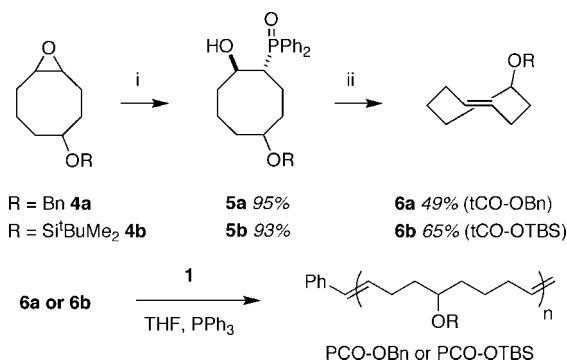
Figure 7. PNb (solid line), M_n = 20 000 g/mol, PDI = 1.01; PNb-*b*-PCO (dashed line), M_n = 81 000 g/mol, PDI = 1.14.

was 139 °C, which is slightly higher than the published values of 129 and 133 °C, respectively.[9,11]

Synthesis of Hydrogenated Norbornene-*b*-polyethylene. Diblock copolymers were synthesized by the sequential addition of monomers. As shown in Scheme 3, the polynorbornene (PNb) block was synthesized using catalyst **1** in the presence of 2 equiv of PPh$_3$ relative to **1** and was subsequently added to a solution containing tCO (0.1 M in THF) and 58 equiv of PPh$_3$ relative to **1**. Shown in Figure 7 are the GPC traces for PNb homopolymer (PNb, solid line) and the PNb-*b*-PCO copolymer (dashed line). The monomodal GPC trace PNb-*b*-PCO indicates the formation of diblock copolymer by living ROMP. The block copolymer was then hydrogenated using the same procedure as was used for the homopolymer, and two melting points of 136 and 143 °C were observed for the polyethylene and pNb blocks, respectively.[39]

Synthesis and ROMP of Functionalized *trans*-Cyclooctene. Functional group tolerant ruthenium metathesis catalysts have allowed for the assembly of a broad array of monodispersed, heteroatom-functionalized, PNb materials.[3,40] Functionalized materials deriving from more flexible backbones have also been synthesized from substituted cyclobutene[10,41] and cyclooctene monomers[42] albeit with higher PDIs than most substituted PNbs. Living ROMP of tCO enables the synthesis of PCOs exhibiting low PDIs and flexible polymer backbones. The incorporation of heteroatom substitution on PCOs with PDIs < 1.1 should allow for access to functionalized materials with physical properties that are not accessible in substituted PNbs.

As shown in Scheme 4, the synthesis of protected 5-hydroxy tCOs can be accomplished according to the method originally described by Shea and co-workers for unsubstituted tCO.[43] Treatment of either epoxycyclooctane **4a** or **4b** with ClPPh$_3$ and Li^0 followed by an oxidative workup furnished phosphine oxides **5a** and **5b** in excellent yields as inconsequential, 2:1 mixtures of regioisomers (only one is shown). Elimination of each of the phosphine oxides **5a** and **5b** by treatment with NaH generated the desired *trans*-cyclooctenes **6a** and **6b** in good to moderate yields, in each case as a 2:1 mixture of diastereomers.

Scheme 4. Synthesis and Polymerization of Hydroxy-Functionalized tCOs[a]

R = Bn **4a**   **5a** *95%*   **6a** *49%* (tCO-OBn)
R = Si^tBuMe₂ **4b**   **5b** *93%*   **6b** *65%* (tCO-OTBS)

6a or 6b →(1, THF, PPh₃)→ PCO-OBn or PCO-OTBS

[a] Key: (i) ClPPh₂, Li⁰, THF, 23 °C, 24 h; H₂O₂, AcOH, 2 h, 2:1 mixture of regioisomers; (ii) NaH, DMF, 0 °C, 2:1 mixture of diastereomers.

Table 6. Effect of Increasing $[M]_0/1$ for Polymerization of 6a and 6b[a]

entry	monomer	$[M]_0/1$	$M_n (\times 10^3$ g/mol)	M_n (theo) $(\times 10^3$ g/mol)	PDI	% yield
20	**6a**	200	41	43	1.06	68
21	**6a**	400	110	87	1.03	82
22	**6a**	600	163	130	1.03	88
23	**6a**	800	200	173	1.02	84
24	**6a**	1000	266	216	1.02	93
25	**6b**	200	55	48	1.02	48
26	**6b**	400	117	96	1.02	93
27	**6b**	600	170	144	1.02	85
28	**6b**	800	249	192	1.02	85
29	**6b**	1000	321	240	1.02	93

*[a] Polymerization conducted with PPh₃/**1** = 60, $[M]_0$ = 0.25 M, at 23° C for 5 min.*

Scheme 5. Synthesis of a Functionalized PCO Diblock Copolymer[a]

PCO-OBn-*b*-PCO-OTBS
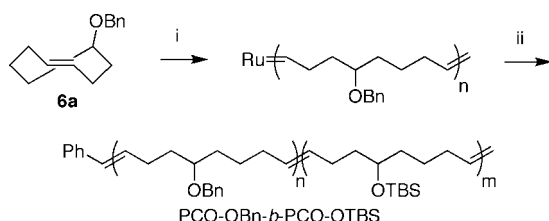
*[a] Key: (i) **1**, [PPh₃]/**1** = 60, $[M]_0$ = 0.25 M in THF, 5 min, 23 °C; (ii) **6b**, 0.25 M in THF, 5 min.*

Polymerization using catalyst **1** of each of the resulting *trans*-cyclooctenes **6a** and **6b** (or tCO-OBn and tCO-OTBS, respectively) in the presence of 60 equiv of PPh₃ relative to catalyst **1** in THF afforded functionalized polycyclooctenes PCO–OBn and PCO–OTBS with low PDIs (Table 6). Good control over the molecular weight based on the ratio of monomer to catalyst **1** was observed for the polymerization of both monomers. The living ROMP of heteroatom-functionalized momoners **6a** and **6b** demonstrates the generality and mild nature of this polymerization method and introduces tCOs as a new class of monomers suitable for the construction of linear narrowly dispersed PCOs.

Di- and triblock copolymers of **6a** and **6b** were then synthesized to further demonstrate the living nature of the polymerization of functionalized tCOs. As shown in Scheme 5, a diblock copolymer was synthesized by addition of initiator **1** to a solution of **6a** and 60 equiv of PPh₃ (relative to **1**) in THF followed 5 min later by addition of a solution of **6b** in

THF (0.25 M) to the reaction mixture. Low PDIs were observed for the synthesis of block copolymers of varying molecular weights (Table 7). ABA triblock copolymers were also synthesized by adding a solution of **6a** to the growing polymer chain of PCO-OBn-*b*-PCO-OTBS (entries 33 and 34, Table 7). Functionalized, monodispersed, polycyclooctene block copolymers have not previously been available through ROMP, and the introduction of substituted tCOs allows for the synthesis of a new class of hydroxylated materials. We anticipate that these differentially protected PCO block copolymers will enable the selective introduction of biologically active molecules to the PCO scaffold while maintaining control over the material properties.

Conclusions

The living ROMP of tCO was successfully performed with catalyst **1** in the presence of PPh₃. The ratio of PPh₃ to **1** as well as the reaction solvent played a crucial role in the living polymerization of this highly strained cyclic alkene. By varying reaction conditions, competing secondary metathesis reactions during ROMP were suppressed, leading to low PDI polymers and precise molecular weight control. Hydrogenation of polycyclooctene yielded low PDI HDPE, and block copolymers were also synthesized and hydrogenated, yielding polymers with linear polyethylene blocks. Furthermore, the functional group tolerance of catalyst **1** was exploited to polymerize *trans*-cyclooctene derivatives. These results have thus enabled the synthesis of di- and triblock copolymer architectures that include blocks of functionalized polycyclooctene.

Experimental Section

General Methods. NMR spectra were recorded on a Varian Mercury 300 (300 MHz for ¹H and 74.5 MHz for ¹³C). All NMR spectra were recorded in CDCl₃, referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and dn/dc values were obtained for each injection by assuming 100% mass elution from the columns. Differential scanning calorimetry (DSC) was carried out simultaneously on a Perkin-Elmer Pyris1 under a flow of helium at a heating rate of 10 °C/min.

Materials. THF and CH₂Cl₂ were dried by passage through solvent purification columns[44] and passed through basic alumina. Triphenylphosphine (PPh₃) was obtained from Alfa Aesar and recrystallized from ethyl acetate prior to use. Norbornene was sublimed prior to use and acetone (technical grade) was dried over calcium sulfate and filtered prior to use as a solvent. All other chemicals were obtained from Aldrich and used as received. Ruthenium catalysts (PCy₃)₂(Cl)₂RuCHPh,[19] (PPh₃)₂(Cl)₂RuCH-Ph,[19] (H₂IMes)(3-Br-pyr)₂(Cl)₂RuCHPh,[17] and *trans*-cyclooctene[43] were all synthesized according to literature procedures. All *trans*-cyclooctenes were handled using glassware that had been treated with 10% Me₂SiCl₂ in PhCH₃ for 1 h, rinsed with PhCH₃ and oven-dried overnight. Polycyclooctene (PCO) and polynorbornene (PNb) have also previously been characterized.[32,45,46]

General Polymerization Procedure for Polycyclooctene and Functionalized Polycyclooctenes. A 4 mL vial with a septum cap was charged with the desired amount of *trans*-cyclooctene and a stirbar under a flow of argon. Solvent (THF or CH₂Cl₂) in the necessary concentration and PPh₃ (see tables for exact amounts) were added to the vial. A stock solution of catalyst was quickly added to the vigorously stirring monomer solution via syringe under an argon atmosphere. After stirring at 23 °C for 10 min, ethyl vinyl ether (~0.2 mL) was added and the reaction was allowed to stir for 1 h. The polymeric product was then precipitated by dropwise addition of the reaction mixture into 100 mL of vigorously stirring

Table 7. AB and ABA Block Copolymers of 6a and 6b[a]

entry	monomer A ($[M]_0/1$)	monomer B ($[M]_0/1$)	monomer A ($[M]_0/1$)	M_n ($\times 10^3$) g/mol	M_n(theo) ($\times 10^3$ g/mol)	PDI	% yield
30	**6b** (150)	**6a** (150)		78	69	1.04	85
31	**6a** (200)	**6b** (200)		102	91	1.04	88
32	**6a** (400)	**6b** (200)		165	135	1.03	86
33	**6a** (200)	**6b** (200)	**6a** (200)	151	135	1.04	79
34	**6a** (200)	**6b** (400)	**6a** (200)	215	183	1.05	89

[a] Polymerization conducted with $PPh_3/1 = 60$, $[M]_0 = 0.25$ M at 23 °C for 5 min after each monomer addition.

acetone (PCO) or methanol (functionalized PCO) and a white precipitate was formed. The polymer was washed multiple times with acetone or methanol and dried in vacuo overnight. See the tables for molecular weights and yields.

PNb-*b*-PCO Block Copolymer. A 4 mL vial with a septum cap was charged with the desired amount of norbornene, a stirbar and THF (0.5 M) under a flow of argon. A second 20 mL vial was charged with a stirbar and the desired amount of tCO and THF (0.1 M). A 2 equiv sample of PPh_3 relative to catalyst was added to the vial containing norbornene and 58 equiv of PPh_3 relative to catalyst was added to the vial containing tCO. A stock solution of catalyst was quickly added to the vigorously stirring norbornene solution via syringe while under argon. After stirring at room temperature for 10 min under a flow of argon, a desired amount of solution was taken up in syringe and added to the vigorously stirring solution of tCO (0.1 M in THF with 58 equiv PPh_3). The remaining norbornene solution and block copolymer reaction were quenched after 10 min with ethyl vinyl ether (0.2 mL) and allowed to stir for one hour at room temperature. Each reaction mixture was then precipitated into two separate flasks containing vigorously stirring acetone (100 mL). A white precipitate was observed for each. The polymers were then washed multiple times with acetone and dried in vacuo overnight. PNb: $M_n = 20\,000$ g/mol, PDI = 1.01, yield = 90% (13% *cis* olefin). PNb-*b*-PCO: $M_n = 81\,000$ g/mol, PDI = 1.14, yield = 90%.

General Hydrogenation Procedure. In a typical experiment, an oven-dried 100-mL round-bottom flask was charged with a stir bar and polymer, tosyl hydrazide (3.5 equiv per double bond), $^nPr_3N$ (1 equiv per tosyl hydrazide), xylenes (0.2 M), and a trace amount of BHT (~10 mg). The mixture was degassed by pulling high vacuum on the solution for about 45 s. Under an argon atmosphere, the flask was fitted with a reflux condenser, and the reaction was heated to reflux (150 °C) for 7 h. The reaction mixture was then cooled to room temperature and precipitated into stirring acetone. The white precipitate was washed several times with acetone and then dried in vacuo for several hours. HDPE yield = 95%, PNb-*b*-PCO yield = 94%.

5-(Benzyloxy)-1,2-epoxycyclooctane, 4a. To a stirred solution of 4,5-epoxycyclooctanol[47] (750 mg, 5.28 mmol) in 11 mL of THF was added tBuOK (935 mg, 7.91 mmol). The mixture was stirred at 23 °C until all solids had dissolved (about 10 min), and then benzyl bromide (1.25 mL, 10.56 mmol) was added via syringe. The resulting yellow slurry was stirred vigorously for 2 h and then quenched by the addition of 2 mL of MeOH followed by 30 mL of H_2O. The contents were transferred to a separatory funnel and extracted with 75 mL of EtOAc. The organic phase was isolated, and the aqueous layer was extracted with 2 × 50 mL of EtOAc. The combined organic fractions were combined and washed with 1 × 30 mL of saturated aqueous $NaHCO_3$ followed by 1 × 30 mL of saturated aqueous NaCl, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of this material by chromatography on silica gel (10% EtOAc/hexanes) afforded **4a** (1.04 g, 85% yield) as a colorless oil. TLC $R_f = 0.30$ (5% EtOAc/hexanes). ^1H NMR: δ 7.48–7.15 (m, 5H), 4.55 (d, $J = 11.7$ Hz, 1H), 4.48 (d, $J = 11.7$ Hz, 1H), 3.60–3.41 (m, 1H), 2.95–2.77 (m, 2H), 2.31–1.80 (m, 5H), 1.74–1.12 (m, 5H) ppm. ^{13}C NMR: δ 138.84, 128.46, 127.56, 127.52, 79.71, 70.60, 55.16, 55.09, 34.19, 30.87, 28.69, 23.98, 22.56 ppm. HRMS (M + H): calculated, 233.1544; found, 233.1542.

5-(tert-Butyldimethylsiloxy)-1,2-epoxycyclooctane, 4b. To a stirred solution of 4,5-epoxycyclooctanol (593 mg, 4.17 mmol) in 4 mL

of DMF was added imidazole (369 mg, 5.42 mmol) followed by *tert*-butyldimethylchlorosilane (817 mg, 5.42 mmol). The resulting mixture was stirred at 23 °C for 15 h and then quenched by the addition of 10 mL of H_2O. The contents were transferred to a separatory funnel and extracted with 50 mL of Et_2O. The layers were separated, and the ethereal layer was washed with 3 × 10 mL of H_2O followed by 1 × 15 mL of saturated aqueous NaCl. The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of this material by chromatography on silica gel (4% EtOAc/hexanes) furnished **4b** (895 mg, 84% yield) as a colorless oil. TLC $R_f = 0.49$ (5% EtOAc/hexanes). ^1H NMR: δ 3.90 (td, $J = 8.8$, 4.3 Hz, 1H), 2.97–2.78 (m, 2H), 2.14 (m, 1H), 2.02 (m, 1H), 1.84–1.57 (m, 5H), 1.52–1.20 (m, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H) ppm. ^{13}C NMR: δ 71.93, 55.44, 55.38, 36.33, 34.32, 27.72, 25.98, 22.65, 22.55, 18.29, −4.68, −4.75 ppm. HRMS (M − H): calculated, 255.1768; found, 255.1780.

5-(Benzyloxy)-2-(diphenylphosphoryl)cyclooctanol, 5a. Li^0 wire (303 mg, 43.7 mmol, 4 equiv) was rinsed with hexanes, patted dry and quickly weighed into a flame-dried flask with stirbar. The flask was purged with argon and then charged with 35 mL of THF. Chlorodiphenylphosphine (2.07 mL, 11.2 mmol, 1.3 equiv) was then added dropwise, and the mixture was stirred vigorously at 23 °C for 18 h during which time the solution became reddish brown. The remaining Li^0 wire was carefully removed from the flask, and a solution of 5-(benzyloxy)-1,2-epoxycyclooctane **4a** (2.0 g, 8.62 mmol) in 13 mL of THF was added via cannula. An additional 4 mL of THF was used to ensure complete transfer of the epoxide. The resulting mixture was stirred for an additional 24 h during which time the color changed to light yellow. The reaction mixture was cooled to 0 °C and quenched by the addition of glacial AcOH (0.64 mL, 11.2 mmol, 1.3 equiv) and H_2O_2 (30% aqueous, 1.2 mL, 11.2 mmol, 1.3 equiv). The mixture was removed from the ice bath, stirred vigorously at 23 °C for 2 h and then transferred to a separatory funnel with 100 mL of CH_2Cl_2 and 50 mL of H_2O. The layers were separated, and the aqueous layer was extracted with an additional 2 × 50 mL of CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford a white foam. Purification of this material by chromatography on silica gel (100% EtOAc) afforded phosphine oxide **5a** (3.56 g, 95% yield) as an inseparable 2:1 mixture of regioisomers as a white powder. TLC $R_f = 0.23$ (100% EtOAc). ^1H NMR (mixture of regioisomers): δ 7.79–7.25 (m, 15H), 4.63–4.40 (m, 2H), 4.20–3.99 (m, 1H), 3.60–3.44 (m, 1H), 3.13–2.94 (m, 1H), 2.18–1.44 (m, 9H), 1.29–1.14 (m, 0.33H), 1.12–0.94 (m, 0.67H) ppm.

5-(tert-Butyldimethylsiloxy)-2-(diphenylphosphoryl)cyclooctanol, 5b. Compound **5b** was synthesized according to the procedure described for phosphine oxide **5a** using 5-(*tert*-butyldimethylsiloxy)-1,2-epoxycyclooctane (1.60 g, 6.25 mmol). Purification by chromatography on silica gel (gradient elution: 66% → 100% EtOAc/hexanes) furnished phosphine oxide **5b** (2.65 g, 93% yield) as a 2:1 mixture of diastereomers. TLC $R_f = 0.50$ (100% EtOAc); ^1H NMR (2:1 mixture of regioisomers): δ 7.83–7.43 (m, 10H), 5.40 (br s, 0.66H), 5.04 (br s, 0.33H), 4.17–3.95 (m, 1H), 3.87–3.71 (m, 1H), 3.08–2.81 (m, 1H), 2.06–1.42 (m, 9H), 1.31–1.18 (m, 0.33H), 1.13–0.97 (m, 0.67H), 0.89 (s, 6H), 0.86 (s, 3H), 0.05 (s, 2H), 0.04 (s, 2H), 0.03 (s, 1H), 0.01 (s, 1H) ppm.

5-(Benzyloxy)-1,2-E-cyclooctene, 6a. NaH (95%, 250 mg, 9.84 mmol, 1.2 equiv) was weighed into a round-bottomed flask with stirbar in an N_2-filled glovebox. The flask was sealed with a rubber septum and removed from the glovebox. The flask was then charged

with 30 mL of DMF and cooled in an ice bath. To the suspension of NaH was then cannulated a solution of phosphine oxide **5a** (3.56 g, 8.20 mmol) in 8 mL of DMF. An additional 3 mL of DMF was used to ensure complete transfer of the phosphine oxide. The resulting mixture was allowed to gradually warm to 23 °C over 2 h with vigorous stirring. After this time, the solution was cooled to 0 °C and 30 mL of water was added carefully. The mixture was transferred to a separatory funnel with 150 mL of pentane, and the layers were separated. The pentane layer was washed with 3×50 mL of water, dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford *trans*-cyclooctene **6a** (836 mg, 47% yield) as a colorless oil as a mixture of two diastereomers. ^1H NMR (2:1 mixture of regioisomers): δ 7.41−7.24 (m, 5H), 5.78−5.46 (m, 0.66H), 5.65−5.29 (m, 0.33H), 4.58−4.35 (m, 2H), 3.73−3.64 (m, 0.66H), 3.15−3.07 (m, 0.33H), 2.48−2.14 (m, 4H), 2.10−1.73 (m, 4H), 1.63−1.43 (m, 1.33 H), 1.35−1.18 (m, 0.67 H) ppm. ^{13}C NMR: δ 139.62, 139.06, 136.04, 135.50, 132.34, 131.42, 128.43, 128.32, 127.58, 127.45, 127.20, 127.00, 85.11, 74.10, 70.34, 70.18, 40.97, 40.38, 38.11, 34.74, 34.64, 33.15, 33.09, 31.79, 30.00, 27.77 ppm. HRMS: calculated, 216.1514; found, 216.1510.

5-(tert-Butyldimethylsiloxy)-1,2-E-cyclooctene, 6b. Synthesized according to the procedure described for *trans*-cyclooctene **6a** starting from phosphine oxide **5b** (2.65 g, 5.78 mmol). *trans*-Cyclooctene **6b** (905 mg, 65% yield) was obtained as a 2:1 mixture of diastereomers and as a colorless oil. ^1H NMR (2:1 mixture of regioisomers): δ 5.70−5.30 (m, 2H), 4.01 (dd, *J* = 10.2, 5.4 Hz, 0.67H), 3.43−3.36 (m, 0.33H), 2.49−1.47 (m, 9H), 1.30−1.13 (m, 1H), 0.94 (s, 6H), 0.87 (s, 3H), 0.032 (s, 4H), 0.026 (s, 1H), 0.01 (s, 1H) ppm. ^{13}C NMR: δ 135.79, 135.46, 132.44, 131.41, 78.56, 67.60, 44.88, 43.94, 41.96, 35.19, 34.77, 34.56, 32.99, 31.26, 29.64, 27.70, 26.14, 26.06, 18.38, 18.29, −4.45, −4.50, −4.70, −4.81 ppm. HRMS: calculated, 240.1910; found, 240.1912.

PCO−OBn (Table 6, Entry 20). The product was recovered as a white spongy solid. ^1H NMR: δ 7.39−7.21 (m, 5n H), 5.44−5.29 (m, 2n H), 4.48 (s, 2n H), 3.43−3.33 (m, 1n H), 2.17−1.90 (m, 4n H), 1.68−1.32 (m, 6n H) ppm.

PCO−OTBS (Table 6, Entry 25). The product was recovered as a white spongy solid. ^1H NMR: δ 5.43−5.29 (m, 2n H), 3.67−3.59 (m, 1n H), 2.13−1.86 (m, 4n H), 1.52−1.23 (m, 6n H), 0.89 (s, 9n H), 0.04 (s, 6n H) ppm.

PCO−OBn-b-PCO−OTBS (Table 7, Entry 31). The product was recovered as a white spongy solid. ^1H NMR δ 7.34−7.27 (m, 5n H), 5.45 - 5.27 (m, 4n H), 4.48 (s, 2n H), 3.68−3.59 (m, 1n H), 3.40−3.42 (m, 1 nH), 2.16−1.85 (m, 8 nH), 1.67 - 1.25 (m, 12n H), 0.89 (s, 1n H), 0.041 (s, 3n H), 0.035 (s, 3n H) ppm.

PCO−OBn-b-PCO-OTBS-b-PCO−OBn) (Table 7, Entry 33). The product was recovered as a white spongy solid. ^1H NMR δ 7.35−7.29 (m, 10n H), 5.42−5.30 (m, 6n H), 5.48 (s, 4n H), 3.68−3.60 (m, 1n H), 3.41−3.33 (m, 2n H), 2.15−1.91 (m, 12n H), 1.66−1.28 (m, 18n H), 0.89 (s, 9n H), 0.04 (s, 6n H) ppm.

Supporting Information Available: Figure showing a DSC chart for hydrogenated polyethylene and PNb-*b*-PCO. This material is available free of charge via the Internet at http://pubs.acs.org.

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