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 PPh$_3$ in THF leads to the formation of narrowly dispersed polycyclooctene (PCO). The presence of PPh$_3$ 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 contaminants. 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 of 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. Polycyclobutene, with a PDI of 1.1, has been prepared using well-defined tungsten catalysts in the presence of trimethylphosphine (PMe$_3$). Polymers have been shown to limit secondary metathesis (vide infra). Similarly, Register and coworkers have shown the living ROMP of low strain cyclopentene with well-defined molybdenum alkylidene initiators, also in the presence of PMe$_3$. Despite the benefits of using a commercially available catalyst and monomer, the low strain of cyclopentene forces the polymerizations to be conducted at 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. Nuckolls and co-workers recently reported the living polymerization of trans, cis-dibenzo[a,e]cyclooctatetraene. Polymers having PDIs < 1.1 were formed when the reaction was conducted in the presence of 3 equiv of tricyclohexylphosphine (PCy$_3$). It was also noted that cis, cis-dibenzo[a,e]cyclooctatetraene 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, which lowers its activity for living ROMP. In contrast, tCO has a ring strain of 16.7 kcal/mol (Figure 2). If secondary metathesis can be prevented, highly strained tCO will be excellent candidate for living ROMP polymerization.

**ROMP of trans-Cyclooctene**

The ROMP of tCO was investigated with several well-known ROMP initiators (Scheme 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$_2$Cl$_2$. 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 $k_i$ 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 $[M]_0$/$k_i$. 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 $k_i$ of catalyst 2 relative to both catalysts 1 and 3. The observed high molecular weight polymer was the kinetic product resulting from a relatively low $k_i/k_p$. 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 (PPh$_3$). 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.\textsuperscript{20,21} We therefore decided to add excess PPh$_3$ 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.\textsuperscript{22} Entries 1–7 in Table 2 depict our efforts to reduce secondary metathesis in the polymerization of tCO by varying equivalents of PPh$_3$ 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]/[I], and the PDIs decreased. However, even as the equivalents of PPh$_3$ 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.\textsuperscript{8,11} Register later demonstrated that acyclic/secondary metathesis competes with ROMP in forming the observed high molecular weight polymers.\textsuperscript{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.\textsuperscript{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.\textsuperscript{20,24–26} For example, THF has been used to slow the polymerization of cyclooctatetraene and also limit secondary metathesis.\textsuperscript{27} We have previously observed that catalyst 1 initiates faster and is less prone to secondary metathesis in solvents such as THF.\textsuperscript{20,24} Furthermore, when polymerizations are conducted with early transition metal metathesis catalysts and excess phosphine in THF, secondary metathesis is also suppressed.\textsuperscript{8} More recently, Register and co-workers were able to show that the addition of a small amount THF limited the secondary metathesis in the ROMP of cyclopentene.\textsuperscript{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]/[I]. 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]/[I]). 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 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 \([M]_c\). Hocker and co-workers showed that no polymers are formed until the monomer concentration of cis-cyclooctene exceeds 0.21 M. As a result, it has been difficult to synthesize ultra high molecular weight PCO \((M_n > 100000 \text{ g/mol})\) 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 and linear oligomers are formed. Furthermore, it has been shown that critical monomer concentration is directly related to monomer ring strain. 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 \([M]_c/1\).

**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. 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. 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. 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. 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 PPh₃, contained 56% cis olefin and exhibited a Tᵥ 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 xylene,¹⁹,⁴³–⁴⁸ and yielded linear, narrowly dispersed HDPE. The Tᵥ determined for HDPE 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 PPh₃ relative to 1 and was subsequently added to a solution containing tCO (0.1 M in THF) and 58 equiv of PPh₃ 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 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 CIPPh₃ and Li₅0 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. 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 monomers 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 PPh$_3$. The ratio of PPh$_3$ 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 $^1$H and 74.5 MHz for $^{13}$C). All NMR spectra were recorded in CDCl$_3$, referenced to residual proteo species. Gel permeation chromatography (GPC) was carried out in THF on two PLgel 10μm 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 CH$_2$Cl$_2$ were dried by passage through solvent purification columns$^{44}$ and passed through basic alumina. Triphenylphosphine (PPh$_3$) 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 (PCy$_3$)$_2$(Cl)$_2$RuCHPh$_2$,$^{19}$ (PPh$_3$)$_2$(Cl)$_2$RuCHPh$_2$,$^{19}$ (H$_2$IMes)(3-Br-pyr)$_2$(Cl)$_2$RuCHPh$_2$,$^{17}$ and *trans*-cyclooctene$^{43}$ were all synthesized according to literature procedures. All *trans*-cyclooctenes were handled using glassware that had been treated with 10% Me$_2$SiCl$_2$ in PhCH$_3$ for 1 h, rinsed with PhCH$_3$ 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 CH$_2$Cl$_2$) in the necessary concentration and PPh$_3$ (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 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 PPh₃ relative to catalyst was added to the vial containing norbornene and 58 equiv of PPh₃ 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 PPh₃). 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: $M_n = 20\,000\,\text{g/mol}$, PDI = 1.01, yield = 90% (13% cis olefin). PNb-b-PCO: $M_n = 81\,000\,\text{g/mol}$, 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), $n$Pr₃N (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 (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 H₂O. 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 NaHCO₃ followed by 1 × 30 mL of saturated aqueous NaCl, dried over Na₂SO₄, 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). $^1$H NMR: $\delta$ 7.48–7.15 (m, 5H), 4.55 (d, $J = 11.7\,\text{Hz}$, 1H), 4.48 (d, $J = 11.7\,\text{Hz}$, 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: $\delta$ 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-butylimidethylchlorosilane (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 H₂O. The contents were transferred to a separatory funnel and extracted with 50 mL of Et₂O. The layers were
separated, and the ethereal layer was washed with 3 × 10 mL of H\(_2\)O 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). \(^{1}\)H 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 acetic acid (0.64 mL, 11.2 mmol, 1.3 equiv) and \(\text{H}_2\text{O}\) (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\(_2\)Cl\(_2\) and 50 mL of H\(_2\)O. The layers were separated, and the aqueous layer was extracted with an additional 2 × 50 mL of CH\(_2\)Cl\(_2\). The combined organic layers were dried over Na\(_2\)SO\(_4\), 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); \(^{1}\)H NMR (2:1 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), 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-(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); \(^{1}\)H NMR (2:1 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-(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\(_2\)SO\(_4\), 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. \(^{1}\)H NMR (2:1 mixture of regioisomers): δ 7.41–7.24 (m, 5H), 7.41–7.24 (m, 5H), 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.
5.78–5.46 (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, 1.33H), 1.35–1.18 (m, 0.67H) ppm. 13C 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. 13C 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, 12 nH), 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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and Notes

16. Formation of a highly substituted trans-cyclooctene by ring-closing metathesis has been demonstrated; in this report, chelation of het-eroatoms on the substrate to the catalyst was proposed to direct for the unusual product formation: Bourgeois D, Pancrazi A, Ricard L, Prunet J. Angew Chem Int Ed 2000;39:726–728.
Figure 1.
Ruthenium olefin metathesis catalysts (Cy = cyclohexyl).
Figure 2.
Relative ring strain for select cyclic olefins (kcal/mol).\textsuperscript{12}
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.
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.
Figure 5.
Molecular weight control by varying [M]₀/1. ROMP of tCO with 1, [M]₀ = 0.5 M with PPh₃/
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.
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 CH₂Cl₂, [M]₀=0.5 M, PPh₃/I =60, at 23 °C; (b) same as part a except in THF. The reactions were stopped at varying time intervals with ethyl vinyl ether.
Figure 7.
PNb (solid line), $M_n = 20000 \text{ g/mol}, \text{PDI} = 1.01$; PNB-$b$-PCO (dashed line), $M_n = 81000 \text{ g/mol}, \text{PDI} = 1.14$. 
Scheme 1.
ROMP of trans-Cyclooctene
Scheme 2.
ROMP of tCO with Excess PPh₃
Scheme 3. Block Copolymers of Norbornene and tCO<sup>a</sup>

<sup>a</sup> (i) [M]<sub>0</sub>/I = 100, PPh<sub>3</sub>/I = 2, 23 °C, 30 min; (ii) added to a solution of tCO in THF [M]<sub>0</sub> = 0.1 M, PPh<sub>3</sub>/I = 58, 23 °C, 10 min; (iii) tosyl hydrazide, nPr<sub>3</sub>N, xylene 150 °C.
Scheme 4. Synthesis and Polymerization of Hydroxy-Functionalized tCOs

Key: (i) ClPPh$_2$, Li$_0$, THF, 23 °C, 24 h; H$_2$O$_2$, AcOH, 2 h, 2:1 mixture of regioisomers; (ii) NaH, DMF, 0 °C, 2:1 mixture of diastereomers.

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Scheme 5. Synthesis of a Functionalized PCO Diblock Copolymer$^a$

$^a$ Key: (i) $1$, [PPh$_3$/I] = 60, [M]$_0$ = 0.25 M in THF, 5 min, 23 °C; (ii) 6b, 0.25 M in THF, 5 min.
Table 1

Polymerization of tCO in CH$_2$Cl$_2$ with [M]$_0$/1 = 300

<table>
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<tr>
<th>run</th>
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<th>$M_n$ ($\times 10^3$ g/mol)$^b$</th>
<th>% yield$^c$</th>
<th>PDI</th>
</tr>
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<td>0.05</td>
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</table>

$^a$Initial Monomer concentration.

$^b$Mn(theo) = 33 $\times 10^3$ g/mol.

$^c$Isolated yields.
### Table 2

Polymerization of tCO with 1 and Increasing PPh$_3$$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>PPh$_3$/1</th>
<th>[M]$_0$/1</th>
<th>$M_n$ ($\times 10^3$ g/mol)</th>
<th>$M_n$(theo) ($\times 10^3$ g/mol)</th>
<th>PDI</th>
<th>% yield</th>
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<td>14</td>
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<td>400</td>
<td>59</td>
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</table>

$^a$Entries 1–7 were conducted in CH$_2$Cl$_2$, [M]$_0$=0.5 M at 23 °C; entries 8–14 were conducted under the same conditions, except in THF.
### Table 3

Effect of Increasing $[M]_0/1^b$

<table>
<thead>
<tr>
<th>entry</th>
<th>$[M]_0/1$</th>
<th>$M_n (\times 10^3 \text{ g/mol})$</th>
<th>$M_n (\text{theo}) (\times 10^3 \text{ g/mol})$</th>
<th>PDI</th>
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<td>19$^a$</td>
<td>3842</td>
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</table>

$^a [M]_0 = 0.05 \, \text{M}.$

$^b$Polymerizations conducted $[M]_0 = 0.5 \, \text{M}$ with $\text{PPh}_3/\text{I} = 60, 23 \, \text{°C}.$
<table>
<thead>
<tr>
<th>solvent</th>
<th>time (min)</th>
<th>$M_n (×10^3 \text{ g/mol})^a$</th>
<th>PDI</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$Cl$_2$</td>
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<td>39</td>
<td>1.10</td>
<td>66</td>
</tr>
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<tr>
<td></td>
<td>10</td>
<td>52</td>
<td>1.08</td>
<td>99</td>
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<tr>
<td>THF</td>
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<td>1.08</td>
<td>90</td>
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<td>52</td>
<td>1.08</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>54</td>
<td>1.08</td>
<td>87</td>
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</tbody>
</table>

$^aM_n(\text{theo})=44 \times 10^3 \text{ g/mol}.$

$^b$Polymerization conducted with $[M]/[I]=400/1$, with $\text{PPh}_3/[I]=60$ at 23 $^\circ$C.
Table 5

Concentration Study

<table>
<thead>
<tr>
<th>solvent</th>
<th>[M]$^a$</th>
<th>$M_n (\times 10^3 \text{ g/mol})^a$</th>
<th>PDI</th>
<th>% yield</th>
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<td>1.16</td>
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$^a$ $M_n$(theo) = 44 $\times 10^3$ g/mol.

$^b$ Polymerization conducted with [M]/I = 400, PPh$_3$/I = 60 at 23°C and for 10 min.
### Table 6

Effect of Increasing [M]₀/1 for Polymerization of 6a and 6b

<table>
<thead>
<tr>
<th>entry</th>
<th>monomer</th>
<th>[M]₀/1</th>
<th>(M_n) (×10⁵ g/mol)</th>
<th>(M_n) (theo) (×10⁵ g/mol)</th>
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<th>% yield</th>
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<tr>
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</table>

*Polymerization conducted with PPh₃/I = 60, [M]₀ = 0.25 M, at 23°C for 5 min.*
Table 7

AB and ABA Block Copolymers of 6a and 6b

<table>
<thead>
<tr>
<th>entry</th>
<th>monomer A ([M]₀/1)</th>
<th>monomer B ([M]₀/1)</th>
<th>monomer A ([M]₀/1)</th>
<th>Mₘ (×10³ g/mol)</th>
<th>Mₘ (theo) (×10³ g/mol)</th>
<th>PDI</th>
<th>% yield</th>
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<tr>
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<td>6a (200)</td>
<td>6b (200)</td>
<td></td>
<td>102</td>
<td>91</td>
<td>1.04</td>
<td>88</td>
</tr>
<tr>
<td>32</td>
<td>6a (400)</td>
<td>6b (200)</td>
<td></td>
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<td>135</td>
<td>1.03</td>
<td>86</td>
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<tr>
<td>33</td>
<td>6a (200)</td>
<td>6b (200)</td>
<td>6a (200)</td>
<td>151</td>
<td>135</td>
<td>1.04</td>
<td>79</td>
</tr>
<tr>
<td>34</td>
<td>6a (200)</td>
<td>6b (400)</td>
<td>6a (200)</td>
<td>215</td>
<td>183</td>
<td>1.05</td>
<td>89</td>
</tr>
</tbody>
</table>

Polymerization conducted with PPh₃/1 = 60, [M]₀ = 0.25 M at 23°C for 5 min after each monomer addition.