Ring-Opening Metathesis Polymerization of Functionalized Cyclooctenes by a Ruthenium-Based Metathesis Catalyst[†]

Marc A. Hillmyer,[‡] Walter R. Laredo, and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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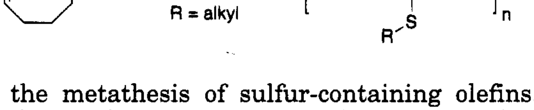
ABSTRACT: The ring-opening metathesis polymerization (ROMP) of a variety of 5-substituted cyclooctenes by the well-defined metathesis catalyst $(PCy_3)_2Cl_2RuCHCHCPh_2$ (**1**) was accomplished. Direct polymerization of functionalized monomers allowed the incorporation of alcohol, ketone, ester, and bromine functionality along the polymer backbone. The polymers were obtained in moderate to good yields. The attempted polymerization of epoxy- and cyano-substituted cyclooctenes by **1** failed. Structures of the polymers were confirmed by IR, ^1H NMR, and ^{13}C NMR spectroscopies. The molecular weight of acetate-containing polymer was controlled by varying the monomer to catalyst ratio and by the addition of a chain transfer agent to the polymerization solution. Hydrogenation of the acetate derivative gave the corresponding ethylene/vinyl copolymer. The thermal properties of the polymers are reported.

Introduction

The incorporation of functional groups (e.g., esters, nitriles, halogens, and alcohols) into the backbones of polymers produced by ring-opening metathesis polymerization (ROMP) has received a great deal of attention.[1,2] The increased tolerance of newly developed early[3−5] and late[6,7] transition metal catalysts toward polar functionalities has facilitated much of the progress. Although there has been considerable success in the ROMP of functionalized cyclic olefins, in most of the reports the monomers employed contain the highly strained bicyclic olefin norbornene. The incorporation of a functional group into a monomer which contains a highly reactive (i.e., strained) cyclic olefin allows the use of a less active catalyst for polymerization.[4] With most early transition metal catalysts, the tolerance of polar functional groups is inversely proportional to the metathesis activity of the catalyst. Polymerization of less strained cyclic olefins requires the use of a more active catalyst and thus precludes the incorporation of functional groups into the monomer. As a result, there are comparatively few reports concerning the ROMP of less strained monocyclic olefins which contain functional groups.[8−11]

Substituted cyclooctenes represent a particularly interesting class of monomers. Their ROMP products are formally terpolymers of butadiene, ethylene, and a substituted ethylene. For example, Basset recently demonstrated the ROMP of a number of 5-(alkylthio)-cyclooctenes by a well-defined tungsten-based metathesis catalyst (eq 1).[12] This is one of the first reports on the metathesis of sulfur-containing olefins. The resulting polymers can be considered as terpolymers of butadiene, ethylene, and vinyl sulfides. Also, Chung reported the polymerization of an alkylboron-substituted cyclooctene.[13] Complete oxidation and hydrolysis of the corresponding borane-substituted polymer yields a terpolymer of butadiene, ethylene, and vinyl alcohol (eq 2).[14] In the monomer the hydroxyl group is masked as a trialkylboron since the tungsten-based metathesis catalyst used in this polymerization is generally intolerant of alcohols. The thermal stability of this terpolymer and its saturated derivatives was significantly better than that of poly(vinyl alcohol).



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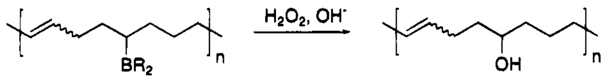

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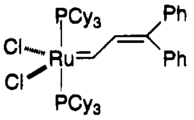
Recently, we described the synthesis of a discrete ruthenium-based metathesis catalyst (**1**) that was active for the polymerization of cyclopentene, cyclooctene, and 1,5-cyclooctadiene (COD).[15] In addition, **1** was active for the metathesis of functionalized acyclic olefins.[15,16] In this paper, the polymerization of cyclooctenes with "unprotected" pendant functional groups catalyzed by **1** is described.



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Results and Discussion

The ruthenium-based metathesis catalyst **1** has been shown to be tolerant of a wide variety of functional groups.[15] This well-defined catalyst will preferentially react with olefins in the presence of polar functional groups such as alcohols, aldehydes, ketones, esters, and ammonium salts. This reactivity has been exploited in the metathesis of such substrates as methyl oleate[15] and has been particularly useful in the catalytic ring-closing metathesis of functionalized dienes (eq 3).[16−20] The ability of **1** to catalyze the metathesis of functionalized acyclic olefins as well as the ROMP of relatively low-

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X = CO_2H, CH_2OH, CHO

[†] Contribution No. 9051.

[‡] Current address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

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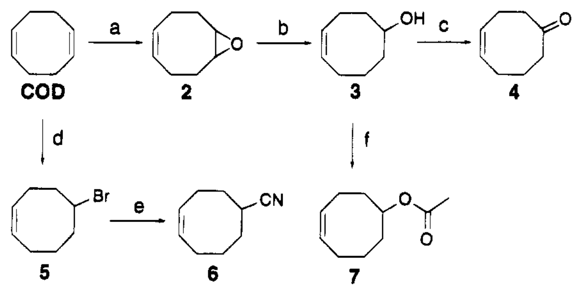
Scheme 1. Synthesis of Substituted Cyclooctenes[a]



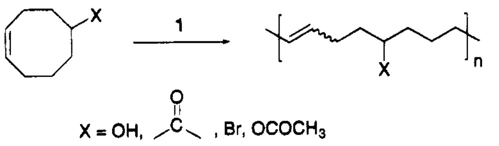
[a] (a) MCPBA/$CHCl_3$ (66%), (b) LAH/THF (100%), (c) PCC/CH_2Cl_2 (95%), (d) HBr/HOAc (74%), (e) NaCN/DMSO (45%), (f) $ClCOCH_3$/pyridine (100%).

Table 1. Polymerization of Substituted Cyclooctenes by 1[a]

entry	monomer	[M]/[1]	t (h)	T (°C)	yield (%)	$10^{-3}\bar{M}_n$[b]	PDI[b]
1	**3**	1044	24	23	65	139	1.6
2	**4**	1037	72	23	47	97.9	1.8
3	**5**	1056	144	23	92	82.4	1.9
4	**7**	1044	72	23	57	96.0	1.9
5	**7**	1041	25	47	85	138	2.4
6	**6**	181	24	23	0		
7	**2**	523	24	23	0		

[a] **1** was dissolved in a minimum amount of CH_2Cl_2, the mixture was added to neat monomer, and the polymerizations were performed under argon. [b] Determined by GPC in THF using polystyrene standards.

strain cyclic olefins prompted this investigation on the ROMP of functionalized cyclooctenes (eq 4).



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Monomer Synthesis. The syntheses of the substituted cyclooctenes employed in this work were easily performed on a multigram scale starting from cyclooctadiene (COD), and all compounds were isolated in moderate to good yield. The synthetic routes to these compounds are illustrated in Scheme 1. All of the monomers synthesized were liquids at room temperature and were purified by distillation or column chromatography. The ruthenium catalyst **1** was also easily synthesized on a multigram scale using standard Schlenk techniques.[15]

Polymerization Procedure. In a typical polymerization, complex **1** was dissolved in a minimum amount of anhydrous, degassed CH_2Cl_2 (e.g., 15 mg of **1** in 200 μL of CH_2Cl_2) and added to a vial containing the monomer (typically 2–3 g) and a magnetic stir bar. The monomer to catalyst ratio employed was typically 1000 to 1. The polymerizations were performed under argon at either room temperature or 45–50 °C. The polymerizations were terminated by the addition of ethyl vinyl ether[21] and isolated by precipitation from an appropriate nonsolvent. The conditions and results are shown in Table 1. The polymerizations are relatively slow compared to those of unsubstituted monomers such as cyclooctene (COD) and cyclopentene.[22] Both the rate of polymerization and polymer yield are significantly increased with increased concentration of the monomer. Best results were obtained when the polymerizations were run in the minimum amount of solvent.[23] Monomers **3**, **4**, **5**, and **7** were successfully polymerized and the corresponding polymers isolated in good yields as rubbery solids. In the case of poly-**7**, an increase in the polymerization temperature increased the yield and molecular weight of the polymer (entries 4 and 5). All of the polymers were readily soluble in common polar organic solvents (e.g., THF, chloroform, and methylene chloride). Poly-**3** was soluble in THF; however, it was significantly more soluble in a 1:1 v/v mixture of chloroform and methanol. Initial attempts to polymerize **2** and **6** failed. There is a precedent for the deactivation of **1** by nitriles,[24] and coordination of the nitrile in **6** by **1** is probably responsible for catalyst deactivation.

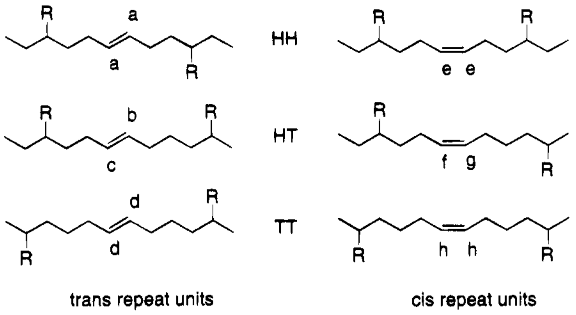


Figure 1. Possible repeat unit structures for the polymers of 5-substituted cyclooctenes. The inequivalent carbons are labeled a–h. HH denotes head-to-head, HT denotes head-to-tail, and TT denotes tail-to-tail regioisomers.

Polymer Characterization. The structures of the polymers obtained (poly-**3**, poly-**4**, poly-**5**, and poly-**7**) were examined by ^1H NMR, ^{13}C NMR, and IR spectroscopies. All of the spectroscopic data were consistent with the repeat units shown in eq 4. The olefinic regions of the ^1H NMR spectra were not well resolved for poly-**4** and poly-**5**; however, in the ^1H NMR spectra of poly-**3** and poly-**7**, two overlapping signals centered at δ 5.25 and 5.32, respectively, were observed. These two signals were assigned to olefinic protons for both cis and trans repeat units. The IR spectrum of each of the polymers contained olefinic out-of-plane C–H bending absorptions for both cis (665–730 cm^{-1}) and trans (960–980 cm^{-1}) olefins, consistent with the presence of both cis and trans repeat units.

The ^{13}C NMR spectra of these polymers were useful in further assigning the microstructure. In the parent polyoctenamer (i.e., from cyclooctene), the olefinic carbon resonances are only sensitive to the configuration of the adjacent sp^2 carbon and not to the configuration of the next nearest double bond. This is also true for polyheptenamer and polypentenamer.[10] Therefore, these three polymers exhibit only two resonances (one cis and one trans) in the olefinic region of their respective ^{13}C NMR spectra. For each of the polymers synthesized in this work, the olefinic region of the ^{13}C NMR spectra contained eight resonances. Although these resonances were not definitively assigned, this multiplicity is consistent with the presence of cis and trans double bonds as well as the presence of the three possible repeat unit regioisomers. The cyclooctenes are asymmetrically substituted, and therefore head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) repeat units are possible. If the ^{13}C olefinic resonances are only sensitive to the configuration of the adjacent sp^2 carbon (analogous to the parent polyoctenamer) and to the position of the two nearest functional groups, then there should be eight resonances in the absence of high regio- or stereospecificity. These different repeat units with the unique carbons labeled a–h are shown in Figure 1. This analysis assumes that the chemical shifts of the olefinic carbons are insensitive to relative *stereochemistry* of the

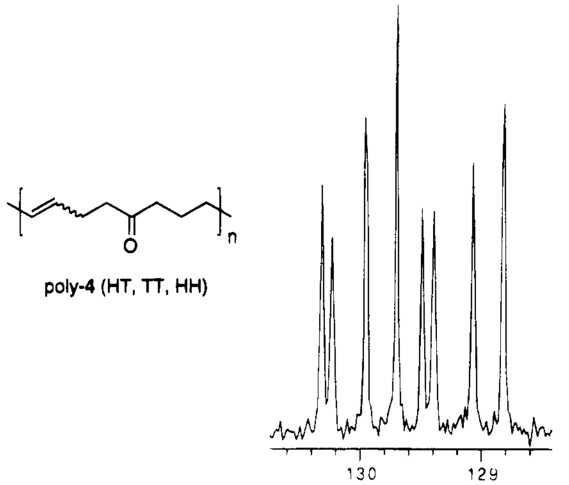


Figure 2. Olefinic region of the ^{13}C NMR spectrum (75 MHz, $CDCl_3$) for poly-**4** (scale is in ppm).

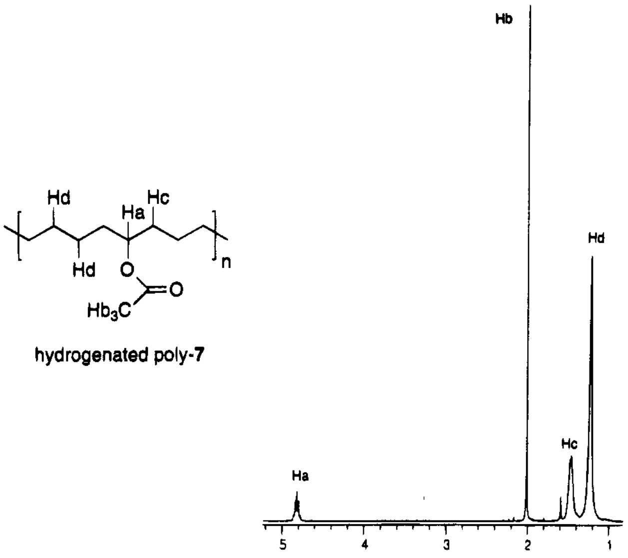
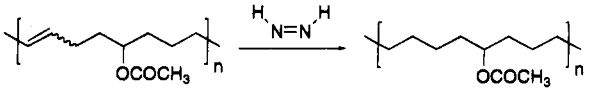


Figure 3. ^1H NMR spectrum (30 MHz, $CDCl_3$) of hydrogenated poly-**7** (scale is in ppm).

two adjacent chiral carbons (racemic or meso diads for the HH and TT regioisomers). This is corroborated by the presence of eight resonances in the olefinic region of the ^{13}C NMR spectrum for poly-**4** (Figure 2). In poly-**4** there are no chiral carbons, and therefore there are a *maximum* of six different repeat units (eight different carbons). If the chemical shifts of the olefinic carbons were also sensitive to meso and racemic diads, an increased number of resonances (which is not observed) would be expected for the polymers derived from the cyclooctene derivatives containing a chiral carbon.

To further establish the microstructure of poly-**7**, the fully saturated version of poly-**7** was also synthesized by stoichiometric hydrogenation with diimide (eq 5).[25]



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The reaction shown in eq 5 was very efficient and effective for the reduction of only the olefinic portion of the poly-**7**. The ^1H NMR spectrum (Figure 3) of this polymer is consistent with the structure shown in eq 3. The ^{13}C NMR of poly-**7** simplified upon hydrogenation. There were no olefinic carbon resonances observed for the hydrogenated polymer. Two equally intense resonances were observed for the methine carbon (δ 74.38 and 74.34), indicating, again, a regioirregular microstructure. Only in the case of a perfectly head-to-tail arrangement of repeat units would one resonance for the methine carbons be expected. Although the regiochemistry of both the parent polymer (poly-**7**) and its hydrogenated version was determined to be irregular, the polyethylene/poly(vinyl acetate) copolymer (hydrogenated poly-**7**) contains an acetate group every eight carbons on average.

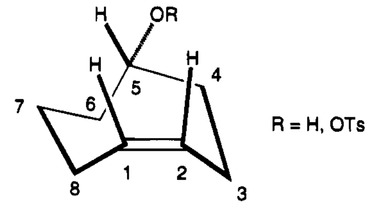

Figure 4. Preferred conformation of two 5-substituted cyclooctenes.

The lack of regiospecificity is not surprising in the ROMP of these 5-substituted cyclooctenes. The substituent on the cyclooctene ring is presumably too far away from the double bond to influence the orientation of the catalyst during the propagation step. This is corroborated by the preferred conformation of 5-substituted cyclooctenes. The dominant conformation of 5-hydroxy-1-cyclooctene (**3**) and the corresponding tosylate (as determined by NMR spectroscopy) is shown in Figure 4.[26] The large substituent on carbon 5 occupies the outside or pseudoequatorial position on the ring, which is in a chair–boat type conformation. This conformation also suggests that in the propagation step, the preferred double bond orientation would be trans (i.e., with the propagating polymer directed up or away from the bottom portion of the ring, i.e., carbons 3 and 8). In fact, high-trans polymers are observed in the polymerization of cyclooctene (which has a similar conformation) with **1**.[15] However, the regiospecificity and stereospecificity in the polymerization of the 5-substituted cyclooctenes described in this work cannot be rationalized based on the propagation step alone. Interchain metathesis results not only in a broadening of molecular weight distribution but also in an equilibration of the regioisomers and double bond orientations in the repeat unit. It is difficult from the data presented here to determine whether the lack of regiospecificity is inherent in the mechanism or results from subsequent isomerization.

The molecular weights of the polymers obtained were generally high, and the polydispersities (PDI's) were between 1.6 and 2.4. Regulation of the molecular weight of poly-**7** was investigated. Although polymerizations catalyzed by **1** are not strictly living due to facile chain transfer to polymer, the total number of polymer chains should be determined by the catalyst concentration and should remain constant. The number-average molecular weight of the polymer should therefore be a linear function of the monomer to catalyst ratio. Indeed, an increase in molecular weight ($\bar{M}_n$) was observed with increasing monomer to catalyst ratio (Table 2), and the relationship between [**7**]/[**1**] and $\bar{M}_n$ is linear at relatively low monomer to catalyst ratios. The molecular weight of poly-**7** can also be lowered if the polymerization of **7** is carried out in the presence of an acyclic olefin such as *cis*-3-hexene (Table 2, entries 5 and 6).[27] The *cis*-3-hexene acts as a chain transfer agent in this polymerization.[10] The use of a chain transfer agent allows the synthesis of relatively low molecular weight

Table 2. Molecular Weight Regulation of Poly-7[a]

sample	[**7**]/[**1**]	$10^{-3}\bar{M}_n$[b]	PDI[b]	yield (%)
1	247	64.1	1.9	88
3	540	96.3	2.1	92
3	1082	126	2.0	90
4	2244	129	2.0	87
5[c]	2688	24.4	1.7	55
6[d]	4700	49.1	1.8	67

[a] Polymerization performed at 50 °C for 24 h. [b] Determined by GPC in THF using polystyrene standards. [c] Polymerized in the presence of *cis*-3-hexene ([**7**]/[*cis*-3-hexene] = 81). [d] Polymerized in the presence of *cis*-3-hexene ([**7**]/[*cis*-3-hexene] = 193).

Table 3. Polymer Thermal Properties[a]

sample	T_g (°C)	T_m, T_{rc} (°C)	T_d (°C)
poly-**3**	10	b	386
poly-**4**	−58	34, 2	404
poly-**5**	−54	*b*	285
poly-**7**	−38	*b*	349
hydrogenated poly-**7**	−38	*b*	345

[a] All values were obtained under an atmosphere of argon at a scan rate of 10 °C/min. [b] No other transition or reaction was observed between the T_g and 100 °C by DSC.

materials while keeping the monomer to catalyst ratio high (entry 6). The molecular weight is determined by the monomer to chain transfer agent (*cis*-hexene) ratio. Increasing this ratio approximately twofold [from 81 (entry 5) to 193 (entry 6)] results in a twofold increase in the number-average molecular weight of the polymer (from 24.4K to 49.1K).

Polymer Properties. The thermal properties of the polymers were analyzed by DSC and TGA. The T_g, T_m, T_{rc}, and the temperature at 10% weight loss (T_d) are given for each polymer in Table 3. The T_g values for all of the polymers were found to be below room temperature. With the exception of poly-**4**, no other transitions or reactions were observed by DSC below 100 °C. The T_g values of poly-**7** and hydrogenated poly-**7** were found to be identical. This behavior has also been observed for polyisoprene and its hydrogenated version (polypropylene-*alt*-polyethylene).[28]

Both poly-**7** and hydrogenated poly-**7** have similar decomposition temperatures and undergo a two-stage weight loss (i.e., a weight loss and then a plateau followed by a second weight loss). Both polymers lose approximately 37 ± 2% of their weight between 300 and 400 °C, and the remaining weight is lost in a subsequent step beginning at ~430 °C. The initial weight loss is accompanied by an exothermic transition in the DSC for both of the polymers. These results are consistent with initial elimination of acetic acid (36% of the repeat unit weight) followed by complete decomposition. Similarly, poly-**5** loses ~41% of its weight between 196 and 374 °C followed by further decomposition beginning at ~430 °C. Elimination of HBr would result in a 43% weight loss and is thought to be the initial decomposition step.

Poly-**4** (CO every eight carbons) has a structure that is intermediate between the perfectly alternating ethylene/carbon monoxide copolymers (CO every three carbons) and the biodegradable random copolymers of ethylene and carbon monoxide (CO every 100 carbons).[29,30] Poly-**4** was the only polymer that exhibited a melting point (T_m = 34 °C). This is surprising since the microstructure of the poly-**4** was determined to be irregular. It appears that there is enough regularity in the sample to induce some degree of crystallinity.[31] The melt transition was reversible, and the T_{rc} was determined to be 2 °C.

Poly-**3** is related to the commercially important poly(vinyl alcohol). The T_g and T_d of poly-**3** were very close to the values reported for Chung's polymer of similar structure obtained via a hydroboration/oxidation procedure.[13] Chung reported a T_g of 11 °C, which is close to the value found for poly-**3** (10 °C). Chung reports the onset of thermal decomposition to be 430 °C.[13] Inspection of Chung's data reveals that the polymer sample lost ~10% of its weight at ~410 °C. This is comparable to the T_d value of 386 °C found for poly-**3**. Unlike Chung's[13] synthesis, the preparation of poly-**3** can be accomplished in one step from **3** to yield the polyethylene–polybutadiene–poly(vinyl alcohol) terpolymer.

Conclusions

The successful ROMP of four cyclooctenes substituted with polar functional groups by the ruthenium-based metathesis catalyst **1** has been demonstrated. The polymers were isolated in good yields, and their structures were investigated by ^{1}H NMR, ^{13}C NMR, and IR spectroscopies. Molecular weights of the polymers were generally high, and predictable molecular weight regulation was demonstrated for one of the derivatives (poly-**7**). Although the regiochemistry and stereochemistry of the repeat units in these polymers were determined to be random, there is, on average, one functional group every eight carbons in these polymers. The thermal properties of all the polymers were determined by DSC and TGA. All of the polymers exhibited glass transitions below room temperature. Three of the polymers synthesized have structures similar to commercially important copolymers of ethylene, namely, ethylene/CO, ethylene/vinyl alcohol, and ethylene/vinyl acetate copolymers.[32] This work represents one of the few successful metathesis polymerizations of functionally substituted cyclooctenes. The success of the polymerization is a direct result of the preferential reactivity of **1** with olefins in the presence of polar functional groups.

Experimental Section

General Considerations. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on a JEOL GX-400 spectrometer (399.65 MHz ^{1}H; 100.40 MHz ^{13}C) or a GE QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. Gas chromatographic analysis was performed on a HP-5890 Series II gas chromatograph with an SE-30 capillary column. Chemical shifts are reported in ppm relative to the solvent resonances. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatograms were obtained on a HPLC system utilizing an Altex Model 110A pump, a Rheodyne Model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed-bed columns, and a Knauer differential refractometer; tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7, and thermogravimetric analysis was accomplished on a Perkin-Elmer TGA-2. Elemental analysis was performed by Fenton Harvey at the California Institute of Technology Elemental Analysis Facility.

Materials. The methylene chloride used in the polymerizations was distilled from CaH_2 under vacuum. All other solvents and common reagents were reagent grade and used without purification. Cyclooctadiene (99%), lithium aluminum hydride, pyridinium chlorochromate, sodium cyanide, *p*-toluenesulfonhydrazide, and *m*-chloroperbenzoic acid were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of cyclooctadiene Monoepoxide (2). A solution of 100 g of 55% *m*-chloroperbenzoic acid (319 mmol) in 900 mL of chloroform was added dropwise over 2 h to 42.8 g of neat 1,5-cyclooctadiene (396 mmol) with stirring. This mixture was allowed to stir at room temperature for 12 h and subsequently filtered to remove the *m*-chlorobenzoic acid. The chloroform layer was washed with aqueous sodium bisulfite, sodium bicarbonate, and sodium chloride solutions. The organic layer was concentrated and purified by column chromatography (silica, 90/10 hexane/ethyl acetate) to yield 26 g (66%) of a clear oil. IR (neat) 2954, 1485, 1446, 938, 862 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.40 (t, 2H), 2.75 (t, 2H), 1.8 (m, 8H).

Preparation of 5-Hydroxy-1-cyclooctene (3). A 1 M THF solution of LAH (44 mL, 44 mmol) was added slowly via syringe to 10.8 g of **2** (87 mmol) in 80 mL of dry THF at room temperature. The reaction was stirred overnight at room temperature under argon, cooled to 0 °C, and quenched with water. The salts were filtered and washed with Et_2O, and the organic fractions were concentrated. The resulting oil was purified by column chromatography (silica, 70/30 hexane/ethyl acetate) to yield 10.5 g (95%) of a colorless oil. GC purity 99.6%; ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 2H), 3.78 (m, 1H), 1.4–2.4 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 130.13, 129.55, 72.75, 37.74, 36.27, 25.64, 24.85, 22.75.

Preparation of Cyclooct-1-en-5-one (4). A solution of 4.0 g of **3** (317 mmol) in 50 mL of dry CH_2Cl_2 was added to 10.2 g of pyridinium chlorochromate (474 mmol) in 60 mL of dry CH_2Cl_2 at room temperature and was allowed to stir for 5 h at room temperature. The reaction mixture was diluted with 60 mL of Et_2O and filtered. The black chromium salts were washed with Et_2O, and the Et_2O washes were combined and concentrated. The resulting brown oil was purified by column chromatography (silica, 80/20 hexane/ethyl acetate) to yield a colorless oil in near-quantitative yield. ^{1}H NMR ($CDCl_3$) δ 5.69 (m, 2H), 2.44 (m, 6H), 2.16 (m, 2H), 1.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 214.81, 130.23, 130.76, 47.28, 40.38, 26.32, 23.94, 21.83.

Preparation of 5-Bromo-1-cyclooctene (5). **5** was synthesized according to the procedure described by Ashby in 74% yield.[33] ^{1}H NMR ($CDCl_3$) δ 5.61 (m, 2H), 4.29 (m, 1H), 2.5–1.9 (m, 8H), 1.71 (m, 1H), 1.52 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 129.55, 129.15, 55.65, 39.73, 37.09, 27.00, 25.24, 25.16.

Preparation of 5-Cyano-1-cyclooctene (6). A mixture of 32 g of sodium cyanide (653 mmol), 25 g of **5** (132 mmol), and 125 mL of DMSO was placed in a round-bottom flask equipped with condenser. The mixture was heated to 110 °C under argon for 2 h, cooled to room temperature, and poured into 200 mL of water. The resulting solution was extracted with Et_2O, and the combined extracts were washed with saturated aqueous LiCl. The solvent was removed under reduced pressure to yield a yellow oil, which was further purified by column chromatography (silica, 90/10 hexane/ethyl acetate) to yield 8.1 g (45%) of 5-cyano-1-cyclooctene. ^{1}H NMR ($CDCl_3$) δ 5.66 (m, 2H), 2.74 (m, 1H), 1.4–2.4 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 130.34, 128.62, 122.99, 31.86, 29.04, 27.88, 26.68, 24.74, 23.10.

Preparation of 5-Acetoxy-1-cyclooctene (7). A solution of 1.0 g of **3** (7.9 mmol) in 10 mL of dry pyridine was cooled to 0 °C. To this solution was added 1.36 of acetyl chloride (17.4 mmol) over 15 min. The reaction was allowed to warm to room temperature and stirred for an additional 1 h. The reaction mixture was diluted with Et_2O and washed with 1 M HCl, saturated aqueous $NaHCO_3$, and water. The organic layer was dried with $MgSO_4$ and concentrated to yield 1.3 g (99%) of a slightly yellow oil. This oil can be further purified by distillation from CaH_2 under reduced pressure (95 °C at 10 mmHg). ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 2H), 4.79 (m, 1H), 2.31 (m, 1H), 2.13 (m, 3H), 1.99 (s, 3H), 1.84 (m, 2H), 1.69 (m, 1H), 1.57 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 170.43, 129.78, 129.58, 75.63, 33.71, 33.65, 21.47, 22.31, 24.80, 25.52. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.82; H, 9.77.

General Polymerization Procedure. An example of the general polymerization procedure is described for the polymerization of **7**. Under an inert atmosphere, a small vial was charged with 2.6 g of degassed **7** (freeze/pump/thaw cycles or an argon purge is acceptable) (15.61 mmol) and a small magnetic stir bar. A solution of 15 mg of **1** (0.015 mmol, [M]/[C] = 1041) in 200 μL of methylene chloride was added to the vial via pipet. The vial was capped and placed in an oil bath at about 45–50 °C. After 2.5 h the red-orange solution was noticeably viscous, and after 5.5 h the contents of the vial were solid. After 24 h the vial was removed from the oil bath and cooled to room temperature. The cap was removed from the vial and 100 μL of ethyl vinyl ether, 10 mL of chloroform, and about 10 mg of 2,6-di-*tert*-butyl-4-methylphenol [butylated hydroxytoluene (BHT)] were added to the vial. The solid dissolved, and the solution became yellow-orange. After about 12 h of stirring, an additional 20 mL of chloroform was added to the solution, and the resulting solution was poured into about 200 mL of methanol. The off-white solid that precipitated was stirred in the methanol until it appeared free of color. The white solid was isolated and dried overnight under vacuum to yield 2.2 g (85%).

Hydrogenation of Poly-7. Poly-**7** (1.2 g, 7.2 mmol of olefin) was dissolved in 40 mL of hot *o*-xylene (~80 °C). The solution was cooled to ~40 °C, and 3.0 g of *p*-toluenesulfonhydrazide (16.1 mmol) and 3.1 g of tributylamine (16.2 mmol) were added. The reaction mixture was heated at reflux for 5 h, allowed to cool to room temperature, and extracted with water (4 × 40 mL). The orange organic layer was poured into methanol, and the polymer precipitated. The polymer was isolated, dissolved in toluene, reprecipitated in methanol, isolated, and dried under vacuum to give 1.0 g (84%) of a light yellow, clear solid.

Polymer Characterization. The polymers were characterized by IR (as thin films on a NaCl plate), ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and C,H analysis. The data are presented below.

Poly-**3**: IR 3358, 3002, 2930, 2849, 1651, 1455, 1337, 1079, 961, 710 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3OD$) δ 5.25 (bm, 2H), 3.68 (bs, 1H), 1.92 (bm, 4H), 1.33 (bs, 6H); ^{13}C NMR ($CDCl_3/CD_3OD$) δ 129.84, 129.65, 129.42, 129.37, 129.3 (shoulder), 129.27, 129.17, 129.05, 70.36, 70.26, 70.16, 48.61, 48.39, 48.18, 47.97, 47.75, 47.54, 47.32, 36.65, 36.57, 36.26, 36.21, 36.12, 32.02, 28.20, 26.65, 26.59, 26.54, 25.19, 25.05, 22.95, 22.92, 22.79. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.30; H, 11.12.

Poly-**4**: IR 3006, 2933, 1711, 1439, 1409, 1369, 1096, 971, 724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.32 (bs, 2H), 2.39 (bs, 4H), 2.23 (bs, 2H), 1.97 (bs, 2H), 1.59 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 210.39, 210.36, 210.31, 210.26, 130.31, 130.23, 129.95, 129.70, 129.49, 129.39, 129.07, 128.81, 42.50, 42.46, 42.41, 42.22, 42.15, 42.12, 42.07, 42.03, 31.92, 31.86, 26.71, 26.65, 26.57, 26.54, 23.60, 23.56, 23.47, 23.37, 21.57, 21.53. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.17; H, 9.97.

Poly-**5**: IR 3004, 2935, 2856, 1442, 1299, 1227, 968, 729, 617, 533 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.42 (bm, 2H), 3.99 (bs, 1H), 1.4–2.2 (bm, 10H); ^{13}C NMR ($CDCl_3$) δ 130.94, 130.56, 130.23, 129.82, 129.73, 129.36, 129.09, 128.54, 57.75, 38.95, 38.83, 38.69, 38.57, 32.64, 31.90, 30.55, 27.59, 27.39, 26.67, 26.58, 25.52, 25.45. Anal. Calcd for $C_8H_{13}Br$: C, 50.82; H, 6.93. Found: C, 52.96; H, 7.32.

Poly-**7**: IR 3005, 2938, 2860, 1740, 1438, 1374, 1244, 1021, 968, 728, 608 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.32 (bm, 2H), 4.84 (bs, 1H), 1.9 (bm, 7H), 1.51 (bm, 4H), 1.32 (bm, 2H); ^{13}C NMR ($CDCl_3$) δ 170.78, 130.35, 130.19, 129.88, 129.77, 129.68, 129.60, 129.31, 129.10, 73.76, 73.73, 34.06, 34.00, 33.93, 33.81, 33.77, 33.64, 32.39, 28.42, 27.00, 26.96, 25.32, 25.24, 25.19, 23.20, 23.16, 21.25. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.19; H, 9.63.

Hydrogenated poly-**7**: IR 2829, 2856, 1737, 1464, 1441, 1372, 1243, 1021 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.82 (m, 1H), 2.01 (s, 3H), 1.46 (bs, 4H), 1.22 (bs, 10H); ^{13}C NMR ($CDCl_3$) δ 170.91, 74.38, 74.34, 34.15, 29.52, 29.48, 25.32, 25.26, 21.27. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.66; H, 10.66.

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