# The Microstructure of Poly(cyclopentene) Produced by Polymerization of Cyclopentene with Homogeneous Ziegler–Natta Catalysts

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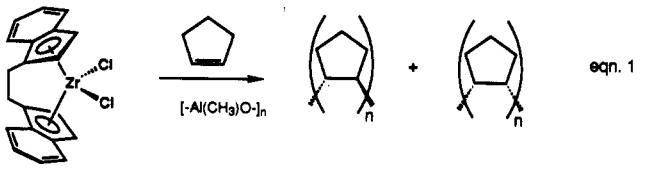
ABSTRACT: The hydro-oligomerization of cyclopentene in toluene solution using [ethylenebis($\eta^5$-indenyl)]-zirconium dichloride (1) or bis(cyclopentadienyl)zirconium dichloride and methylaluminoxane as catalysts was studied. The crude oligomer mixture obtained using the former catalyst was extracted with hot toluene to provide a fraction consisting predominantly of dimer, trimer, and tetramer. Distillation provided trimer of 99% purity. Pure tetramer was precipitated from methanol–toluene as a crystalline solid. Hydro-oligomerization of cyclopentene with zirconocene dichloride as catalyst provided two tetramers, one of which was identical to that produced using the chiral catalyst. The structure of the trimer, including stereochemistry, was established by total synthesis. These results conclusively demonstrate that the original structure assigned to poly(cyclopentene) is incorrect and that enchainment of cyclopentene occurs predominantly by cis-1,3-insertion. A mechanism for the polymerization of cyclopentene using catalyst 1 is discussed.

## Introduction

The polymerization of cyclopentene (and other cyclic monomers) using a soluble catalyst system derived from compound 1 and methylaluminoxane (MAO) was reported several years ago by Kaminsky and co-workers (eq 1). Remarkably, this polymerization proceeds without de-




eqn. 1

1

tectable ring opening of the monomer.[1a] Isotactic poly(cyclopentene) is a highly crystalline polymer that decomposes prior to melting in air and is essentially insoluble in organic solvents. The microstructure assigned to this polymer was based on solid-state $^{13}C$ NMR data. It was concluded that most of the polymer was formed by 1,2-enchainment; it was implied that the structure of this polymer consisted of a copolymer of *trans*- and *cis*-poly(1,2-cyclopentene).

It has occurred to us, and others,[2] that the trans geometry seemed unlikely, since the mechanism of Ziegler–Natta polymerization using both soluble and heterogenous catalysts invariably involves cis insertion for simple, acyclic monomers.[3]

In this paper, we describe the hydro-oligomerization of cyclopentene using catalyst 1, the isolation of pure trimer and tetramer from the mixture of oligomers produced, and the spectral characteristics of the oligomer mixture, the trimer, and the tetramer. The structure of the trimer was established by independent synthesis.

## Results and Discussion

Polymerization of cyclopentene was performed at both room temperature and 60 °C using catalyst 1 under the conditions outlined in the Experimental Section. The IR spectrum, DSC trace (decomposition temperature ~290 °C in air), and wide-angle X-ray diffraction pattern of the product obtained at room temperature were recorded (see the supplementary material). Our IR spectrum differs from that reported[1a] by the *absence* of moderate absorption at ca. 1740 $cm^{-1}$. Since there are no functional groups present that would absorb in this region, nor evidence of strong fundamentals at lower wavenumber, we attribute this band to an impurity. There is clear evidence of terminal unsaturation in the polymer as revealed by absorptions at 3040 (w), 1612 (vw), and 722 (m) $cm^{-1}$. These bands can be assigned to cyclopent-2-en-1-yl end groups in the polymer.[1a,b] The X-ray diffraction maxima and lattice parameters determined from the powder pattern of the polymer were in excellent agreement with those reported by Kaminsky.[1a]

The solution $^{13}C$ NMR spectrum of a trichlorobenzene soluble fraction of the polymer obtained at 60 °C using catalyst 1 is depicted in Figure 1a and resembles that reported recently by Kaminsky.[4]

Hydro-oligomerization of cyclopentene was performed under the conditions outlined in the Experimental Section. The crude hydro-oligomerization product, prepared using catalyst 1, was obtained as a solid, partially soluble in toluene. The crude oligomer mixture was fractionated by extraction with hot toluene. About 60% of the material was insoluble in hot toluene, and the $^{13}C$ NMR spectrum of this oligomer fraction is depicted in Figure 1b. The $^{13}C$ NMR chemical shifts of this fraction are similar to those depicted in Figure 1a, with the exception that additional, relatively intense peaks are observed that correspond to saturated end groups in the oligomer (vide infra).

The fraction soluble in hot toluene contained four main volatile components in a ratio of 41:25:19:15 as determined by GC. These compounds were identified by GC–MS as dimer ($m/z$ 138), trimer ($m/z$ 206), tetramer ($m/z$ 274), and pentamer ($m/z$ 342), respectively. The mixture was fractionally distilled to remove the dimer and provided 0.9 g of trimer (purity 97% by GC) and 0.5 g of tetramer (purity 83% by GC). The trimer was distilled a second time to afford pure product. The $^{13}C$ NMR spectrum of this compound is depicted in Figure 1d (see also Table I). The pure tetramer was isolated by recrystallization from toluene and methanol. The $^{13}C$ NMR spectrum of this compound is portrayed in Figure 1c. Both of these spectra are consistent with these compounds being single stereoisomers.

Further, as can be gleaned from an examination of Figure 1b–d, the $^{13}C$ NMR spectra of the trimer and tetramer are

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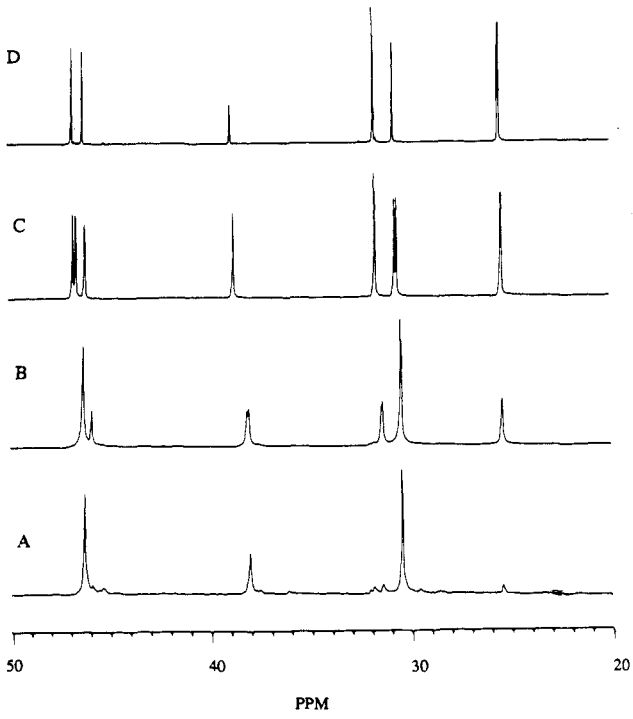



**Figure 1.** $^{13}C$ NMR spectra of cyclopentene oligomers obtained using catalyst 1: (a) trichlorobenzene-soluble fraction from polymerization at 60 °C (1,2,4-trichlorobenzene, 120 °C), (b) hydro-oligomer fraction insoluble in hot toluene (1,2,4-trichlorobenzene, 120 °C), (c) tetramer ($C_6D_6$, 25 °C), (d) trimer ($C_6D_6$, 25 °C).

closely analogous to that of the original hydro-oligomerization mixture, in terms of chemical shifts and intensities of the major resonances observed. This was our first indication that poly(cyclopentene), prepared using catalyst 1, was probably stereoregular as far as the stereochemistry of the two substituents on a given cyclopentane ring was concerned.

It should also be appreciated that the $^{13}C$ chemical shifts of the trimer are not wholly consistent with the structure of *either trans-* or *cis*-1,2-dicyclopentylcyclopentane. The *J*-modulated spin-echo $^{13}C$ NMR spectrum of the trimer and the spectrum obtained under inverse-gated decoupling conditions are depicted in Figure 2a,b, respectively. The two signals at $\delta$ 46.8 and 46.2 ($CDCl_3$, Table I) are due to the methine carbons of the internal and terminal cyclopentane rings, while the four upfield peaks at $\delta$ 32–25 are due to either internal or terminal methylene carbons as determined by comparison to the chemical shifts assigned to dicyclopentyl (Table I).[5] The single peak due to a methylene carbon located at $\delta$ 38.8 is not observed in the spectra of either *cis-* or *trans*-1,2-dimethylcyclopentane,[6a] nor for *cis*-1-isopropyl-2-methylcyclopentane.[6b] Also, the signal is not due to a carbon on a monosubstituted cyclopentyl ring; the signals at higher field could be assigned to these carbons by comparison to the spectrum reported for dicyclopentyl (see Table I).[5] In fact, the chemical shifts assigned to the carbons of the central, five-membered ring (see Table I) are somewhat similar to those reported for *cis-* or *trans*-1,3-dimethylcyclopentane[6a] and closely correspond to those of *cis-* or *trans*-1-isopropyl-3-methylcyclopentane.[6b] It therefore seemed probable that the structure of the trimer might have a 1,3-relationship between the pendant cyclopentyl groups.

Extrapolation of carbon shifts from the above model compounds and/or using rules developed by Grant and Paul[7] are not reliable enough for unambiguous identification in most cases. We therefore decided to prepare *cis*-1,3-dicyclopentylcyclopentane (**2**) by a stereochemically unambiguous route to confirm our hypothesis.

The synthesis of compound **2** is outlined in Scheme I. Aldol condensation of cyclopentanone under the reported conditions provided crystalline dienone **3**.[8] Partial hydrogenation provided a mixture of *cis-* and *trans*-2,5-dicyclopentylcyclopentanone (**4** and **5**),[8] which could be separated by flash chromatography. Cis stereochemistry was assigned to the major isomer on the basis of the observation that reduction of compound **4** with $LiAlH_4$ provided two, stereoisomeric alcohols **6a** and **6b**, whereas reduction of compound **5** gave rise to a single isomer **6c**. Alcohols **6a** and **6b** were converted to the corresponding *S*-methyl thiocarbonates **7a** and **7b**, which were transformed to the target molecule **2** via Barton's deoxygenation procedure but using triphenyltin hydride instead of tributyltin hydride.[9]

The spectral characteristics of *cis*-1,3-dicyclopentylcyclopentane (**2**) were identical to that of the trimer isolated from the hydro-oligomerization of cyclopentene using catalyst **1**. From the similarity in $^{13}C$ NMR spectra of the oligomer mixture to that of the trimer (and tetramer), it can also be concluded that the predominant mode of enchainment of cyclopentene in this polymerization is cis-1,3; the structure originally assigned to the polymer is therefore most probably incorrect.

Although the structure of the trimer indicates that the predominant mode of enchainment of cyclopentene is cis 1,3, the relative stereochemistry between rings in the polymer has not been established.

There are two possible stereoisomeric tetramers that result from cis-1,3-enchainment of cyclopentene (**8** and **9**). As can be appreciated from the diagram, the syndiotactic isomer **8** has a 2-fold axis of symmetry whereas the isotactic isomer **9** has an inversion center. That is, compound **8** is chiral whereas its stereoisomer **9** is not.

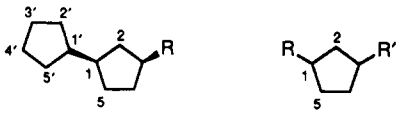
**8** **9**

Although the tetramer isolated from the hydro-oligomerization is crystalline, we have been unable to obtain single crystals suitable for an X-ray structure determination.

Although GC analysis of pure tetramer, obtained from the oligomerization of cyclopentene with catalyst **1**, on a chiral phase[10] gave rise to a single peak, this evidence alone does not distinguish between the two possibilities. Hydro-oligomerization of cyclopentene with the achiral catalyst $Cp_2ZrCl_2$ was performed and two tetrameric products were produced in a ratio of ~1:1 as revealed by GC–MS. One of these compounds had a retention time that was identical to that produced using catalyst **1**. However, GC analysis of this mixture on the chiral column gave rise to only two peaks, not three as expected. Therefore, it is not possible, as present, to determine whether poly(1,3-cyclopentene) is isotactic or syndiotactic.[11]

A plausible polymerization mechanism that accounts for the correct polymer microstructure is outlined in Scheme II.[12] Insertion of monomer into the Zr–H bond of the catalyst produces intermediate **10**. A second, cis insertion provides biscyclopentyl intermediate **11**. Further insertion is likely to be sterically impeded relative to competing processes—i.e. $\beta$-hydride elimination to give olefin hydride complex **12**. Rotation of the olefin about

**Table I**
**$^{13}C$ NMR Data for Trimer, Tetramer, and Various Model Compounds**




A B

| compound | chemical shifts and assignments[a] C(2) | C(1) | C(5) | C(1') | C(2'), C(5') | C(3'), C(4') |
|---|---|---|---|---|---|---|
| trimer (A; R = c-$C_5H_9$)[b] | 39.2 | 47.1 | 31.1 | 46.5 | 32.1 | 25.81, 25.75 |
| bicyclopentyl (A; R = H)[c] | | | | 46.9 | 32.2 | 25.8 |
| trimer (A; R = c-$C_5H_9$)[d] | 38.8 | 46.8 | 30.7 | 46.2 | 31.70, 31.69 | 25.44, 25.40 |
| B (R = *i*-Pr, R' = Me; cis)[e] | 38.7 | 46.4 | 29.9 | | | |
| B (R = *i*-Pr, R' = Me; trans)[e] | 40.8 | 48.5 | 29.9 | | | |
| B(R = R' = Me; cis)[f] | 35.4 | 45.0 | 34.3 | | | |
| B (R = R' = Me; trans)[f] | 33.5 | 43.5 | 35.2 | | | |
| tetramer[b] | 39.2 | 47.1, 46.9 | 31.1, 31.0 | 46.5 | 32.1 | 25.8, 25.7 |

[a] For numbering scheme refer to structure A or B, as appropriate. [b] Spectrum obtained in $C_6D_6$. [c] In $C_6D_6$–see ref 5. [d] Spectrum obtained in $CDCl_3$. [e] In $CDCl_3$–see ref 6b. [f] In $CS_2$–see ref 6a.

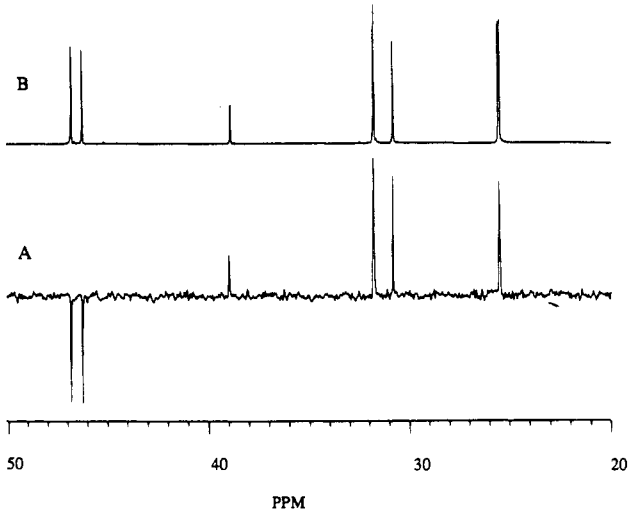



**Figure 2.** $^{13}C$ NMR spectra of the trimer isolated from the hydro-oligomerization of cyclopentene using catalyst 1: (a) *J*-modulated $^{13}C$–H spectrum of the trimer ($CDCl_3$, 25 °C), (b) inverse-gated, decoupled spectrum ($CDCl_3$).

the metal center, followed by cis insertion, provides isomeric biscyclopentyl intermediate **13**. This intermediate is now more favorably disposed for subsequent monomer insertion. Apparently, monomer insertion must be rate-limiting relative to these isomerization processes to account for the observed regioselectivity.

## Conclusions

Polymerization of cyclopentene with soluble Ziegler–Natta catalyst 1 proceeds predominantly by 1,3-enchainment of the monomer and affords isotactic or syndiotactic *cis*-poly(1,3-cyclopentane). Reasonable and satisfactory mechanistic explanations for the polymer microstructure have been developed. It is also conceivable that polymers comprised of other cyclic monomers[1] which are capable of undergoing 1,3-insertion possess a similar microstructure.

## Experimental Section

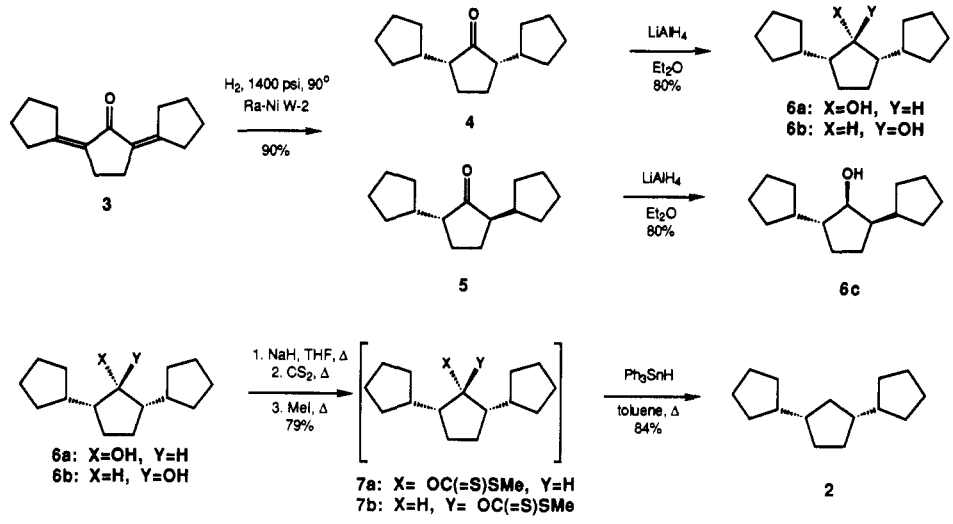
All solvents and chemicals were reagent grade and purified as required. Tetrahydrofuran, diethyl ether, and toluene were dried by distillation from sodium–benzophenone ketyl. Cyclopentene (Fluka >99%) was dried by distillation from $LiAlH_4$. Methylaluminoxane was obtained from Ethyl Corp. as a solution in toluene and the solvent removed under high vacuum to obtain solid MAO used in the polymerizations. Compound 1 was prepared by a literature method.[13] Wide-angle X-ray diffraction data for poly(cyclopentene) were obtained on a Nicolet Siemens D500 diffractometer. DSC analyses of poly(cyclopentene) were conducted using a Perkin-Elmer DSC-4 instrument at a heating rate of 50 °C/min. Calibration was achieved using indium metal.

All synthetic reactions were conducted under an atmosphere of dry nitrogen in dry glassware unless otherwise noted. Compound **3** was prepared by a method described in the literature.[8] $^1H$ and $^{13}C$ NMR spectra were recorded on either a Bruker AM-250 or a AC-200 spectrometer; chemical shifts are referenced with respect to either $C_6D_6$ or $CDCl_3$. IR spectra were obtained using a Nicolet 520 FTIR instrument; spectra were calibrated using poly(styrene) film. Gas chromatography was performed on a Hewlett-Packard 5890 instrument equipped with FID detectors and a 0.25 mm × 30 m J&W Scientific DB-1701 capillary column. GC analyses using a cyclodextrin-based stationary phase[10] were performed on the same instrument using a 0.25 mm × 30 m J&W Scientific CDX-B column. Low- and high-resolution mass spectra were collected on a KRATOS MS-890 machine at the University of Guelph. GC-MS analyses were performed using a Hewlett-Packard 5890 Series II chromatograph equipped with a 5971A Mass Selective Detector and a 0.32 mm × 25 m HP-5 column on loan to the University of Waterloo. Elemental analyses were determined by M.H.W. Laboratories of Phoenix, AZ.

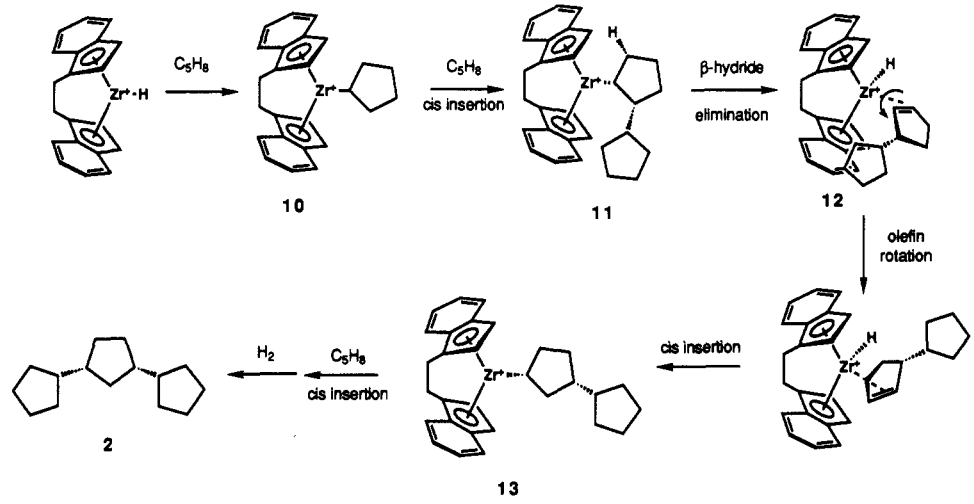
**Hydro-Oligomerization of Cyclopentene with Compound 1.** Hydro-oligomerization of cyclopentene (16.4 g) was conducted in a small Parr autoclave at room temperature in 35 mL of toluene solution containing 300 mg of MAO and 16 mg of [ethylenebis-($\eta^5$-indenyl)]zirconium dichloride. The system was pressurized to 30 psig with hydrogen (Linde), and after 20 h, the vessel was vented and a small volume of methanol was added. The suspension was filtered hot and washed with hot toluene (4 × 50 mL), and the insoluble portion was then washed with methanol and then dried (6.0 g). The toluene-soluble fraction was concentrated to ~100 mL and analyzed by GC. Four major volatile components were present in a ratio of 41:25:19:15. GC–MS analysis of the mixture revealed that these compounds were dimer, trimer, tetramer, and pentamer. The toluene was concentrated in vacuo (15 mmHg) to provide a waxy solid (5.0 g). Further purification was achieved by Kugelrohr distillation. This provided the trimer (0.9 g, 97% pure by GC) and the tetramer [0.5 g, bp 110 °C (0.01 mm Hg), 83% pure by GC]. Further purification of the trimer was achieved by a second distillation (0.05 Torr, 52 °C), to afford the pure product: for $^{13}C$ NMR spectral details, see Table I; $^1H$ NMR (200 MHz, $CDCl_3$) δ 0.7–0.9 (m, 1 H), 1.0–1.35 (m, 6 H), 1.4–2.0 (br m, 19 H); IR (NaCl, neat) 2946 (s), 2906 (sh), 2864 (s), 1464 (sh), 1450 (m), 1362 (vw), 1331 (w), 1304 (sh), 1259 (vw), 932 (w), 894 (w) $cm^{-1}$; mass spectrum (EI), *m/e* 206 ($M^+$). Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.28; H, 12.42.

Pure tetramer was obtained by fractional crystallization from cold toluene–methanol to give a white solid, 99+% pure by GC (mp 89–90 °C): for $^{13}C$ NMR spectral data see Table I; $^1H$ NMR (250 MHz, $CDCl_3$) δ 0.6–0.85 (m, 2 H), 1.0–1.3 (m, 9 H), 1.4–2.0 (br m, 23 H); IR (KBr) 2948 (s), 2902 (sh), 2862 (s), 2837 (sh),

**Scheme I**




**Scheme II**




1711 (m), 1465 (s), 1450 (s), 1445 (s), 1330 (m), 1316 (m), 1299 (m), 1253 (m), 1093 (w), 935 (m), 892 (w), 882 (w) $cm^{-1}$; mass spectrum (EI), *m/e* 274 ($M^+$). Anal. Calcd for $C_{20}H_{34}$: C, 87.52; H, 12.48. Found: C, 87.50; H, 12.41.

GC analysis of this compound on a cyclodextrin-based column gave rise to a single peak with $t_R$ = 32.7 min (190 °C, isothermal).

**Hydro-Oligomerization of Cyclopentene with $Cp_2ZrCl_2$.** The procedure outlined above was followed using 45 mL of toluene, 10.5 mL of cyclopentene, and 8.0 mg of $Cp_2ZrCl_2$ at 25 °C and 0.5 bar of $H_2$ for 1 h. The mixture was quenched with a small volume of methanol and filtered hot (to remove aluminoxane residues) and the toluene was removed in vacuo. The residue (0.5 g) contained trimer, tetramers, and pentamers as revealed by GC–MS of the mixture. Two major tetrameric products were present in a ratio of ~1:1. The mixture was fractionally distilled as above to remove trimer and the residue distilled at 100–120 °C (0.01 mmHg) to give a fraction (0.25 g) predominantly consisting of the two tetramers. GC analysis of these compounds on the chiral GC phase gave rise to two peaks with $t_R$ = 32.0 and 32.7 min, respectively, under the conditions reported above. Coinjection of the pure tetramer, obtained using catalyst 1, with this mixture revealed that the peak with $t_R$ = 32.7 min in the mixture was the same as that produced using catalyst 1: $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 47.1, 32.1, 31.1 and two sets of signals at 46.92, 46.5, 39.20, 30.90, 25.7 and 46.89, 46.3, 39.14, 30.88, 25.6 in a ratio of ~1:1.

**Polymerization of Cyclopentene (at 25 °C).** To 105 mg of MAO in a 100-mL round-bottom flask was added 11.8 mL of toluene containing 2.7 mg of 1 and then 6.2 mL of cyclopentene was added. The mixture was stirred under nitrogen for 24 h prior to being quenched with methanol. The mixture was filtered and the insoluble product was washed with methanol and then dried in vacuo to provide 2.8 g of product. X-ray diffraction, IR, and DSC data are included as supplementary material.

**Polymerization of Cyclopentene (at 60 °C).** To 260 mg of MAO in 40 mL of toluene at 60 °C in a Parr autoclave was added 11.6 mL of cyclopentene. A solution of compound 1 (26.5 mg) in a minimal volume of hot toluene (~5 mL) was then injected by syringe. The mixture was stirred under nitrogen at 60 °C for 4 h prior to being quenched with methanol. The mixture was cooled and filtered and the insoluble product was washed with methanol and then dried in vacuo to provide 6.7 g of product. A 0.25-g portion of this material was extracted with hot 1,2,4-trichlorobenzene, and the $^{13}C$ NMR spectrum of the soluble portion is shown in Figure 1a.

***cis*- and *trans*-2,5-Dicyclopentylcyclopentanone (4 and 5, respectively).** Compound 3 (3.5 g, 16.2 mmol) was suspended in 94 mL of ethanol containing 650 mg of freshly prepared Raney nickel W-2 catalyst in a small, magnetically stirred Parr autoclave. The system was pressurized with hydrogen to 1350 psig and then heated to 86 ± 2 °C with heating tape with stirring. After 5.5 h, the system was cooled to room temperature and then vented. The mixture was dried in vacuo, dissolved in $CHCl_3$, and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to produce 3.5 g of a clear liquid which was a mixture of isomers ($^{13}C$ NMR; 3:1). This mixture was separated by flash chromatography on a silica gel column eluting with hexane–ethyl acetate 9:1. Compound 5 is the first to elute followed by compound 4. Fractions containing compound 5 were combined and concentrated to dryness to give pure material (0.79 g, 23% yield) while those containing compound 4 were combined and concentrated to give pure product 4 (2.36 g, 68% yield).

Compound 4: bp 60–62 °C (0.01 mmHg) $^1$H NMR (250 MHz, $C_6D_6$) δ 0.9–1.15 (m, 2 H), 1.2–1.75 (br m, 15 H), 1.75–2.1 (m, 7 H); $^{13}$C NMR (62.85 MHz, $C_6D_6$) δ 218.90, 52.41, 40.79, 31.15, 30.47, 25.53, 25.47, 25.24; IR (neat, NaCl) 2952 (s), 2868 (s), 1732 (s), 1452 (s), 1355 (w), 1309 (w), 1226 (m), 1176 (m), 1144 (w), 1089 (m), 930 (w) cm$^{-1}$. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.74; H, 10.80. Compound 5: mp 34–35 °C; $^1$H NMR (200 MHz, $C_6D_6$) δ 0.8–2.1 (br complex m, 24 H); $^{13}$C NMR (50.3 MHz, $C_6D_6$) δ 218.78, 53.65, 40.67, 31.09, 29.70, 25.61, 25.36, 25.27; IR (neat, NaCl) 2949 (s), 2867 (s), 1723 (s), 1450 (m), 1154 (w), 754 (w) cm$^{-1}$. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.74; H, 10.66.

***cis,cis*- and *trans,trans*-2,5-Dicyclopentylcyclopentan-1-ol (6a and 6b).** Compound 4 (0.43 g, 1.95 mmol) was added to a 50-mL round-bottom flask and dissolved in 20 mL of dry ether. To this was added $LiAlH_4$ in portions (0.15 g, 3.9 mmol). The mixture was stirred at room temperature for 30 min, after which the mixture was cooled to 0 °C, and water (0.15 mL), 15% aqueous NaOH (0.15 mL), and water (0.45 mL) were added sequentially by syringe. The mixture was filtered through a pad of silica gel, and the filtrate was concentrated in vacuo to provide a solid mixture of the title compounds (0.35 g, yield 80%) with the following spectral characteristics: $^1$H NMR (250 MHz, $C_6D_6$) δ 3.97 (dd, $J$ = 7.2, 3.4 Hz), 3.50 (dd, $J$ = 12.9, 6.8 Hz) in a ratio of 1:4 (total 1 H), 1.1–2.1 (br m, 25 H); $^{13}$C NMR (62.85 MHz, $C_6D_6$) two sets of signals at δ 83.38, 53.28, 44.71, 31.49, 31.13, 27.36, 25.89, 25.34 and 75.82, 52.61, 41.15, 32.27, 32.05, 28.11, 25.63, 25.59 in a ratio of ca. 4:1; IR (KBr) 3400 (br s), 2949 (s), 2863 (s), 1625 (m), 1525 (m), 1450 (s), 1066 (m), 1033 (w), 930 (w) cm$^{-1}$; high-resolution mass spectrum calculated for $C_{15}H_{26}O$ 222.19848, found (EI) 222.19896.

***cis,trans*-2,5-Dicyclopentylcyclopentan-1-ol (6c).** The procedure outlined above was followed using 0.1 g of compound 5 (0.45 mmol) and 35 mg of $LiAlH_4$ (0.9 mmol). After workup as described above the title compound was obtained as the sole product (0.08 g, 79%): $^1$H NMR (250 MHz, $C_6D_6$) δ 3.91 (t, $J$ = 3.4 Hz, 1 H), 1.1–2.1 (br complex m, 25 H); $^{13}$C NMR (62.85 MHz, $C_6D_6$) δ 78.54, 55.67, 51.88, 44.92, 40.22, 32.62, 32.02, 31.70, 31.54, 29.72, 29.52, 25.78, 25.69 (2 C), 25.61; IR (KBr) 3431 (br s), 2955 (s), 2857 (s), 1618 (s), 1524 (m), 1448 (s), 1385 (w), 1339 (w), 1259 (w), 1232 (w), 1188 (m), 1159 (w), 1159 (w), 1091 (w), 1035 (m), 984 (w), 927 (w), 909 (w), 866 (w) cm$^{-1}$; high-resolution mass spectrum calculated for $C_{15}H_{26}O$ 222.19848, found (EI) 222.19890.

***cis*-1,3-Dicyclopentylcyclopentane (2).** A mixture of compounds **6a** and **6b** was converted to their *S*-methyl thiocarbonates **7a** and **7b**, respectively, using the following procedure.[9]

The alcohols (0.23 g, 1.04 mmol) were added to NaH (0.061 g, 2.54 mmol) in 15.0 mL of dry THF, in a two-neck 50-mL round-bottom flask equipped with a condensor. To this was added 2.5 mg of imidazole in 1.1 mL of THF. The mixture was heated under nitrogen to reflux, and after 3 h, carbon disulfide (0.33 mL, excess) was added, and after a further 30 min at reflux, $CH_3I$ (0.33 mL, excess) was added. The solution was allowed to reflux for a further 30 min, at which time the solution was cooled to room temperature and diluted with water. The product was extracted using dichloromethane, which was washed with dilute HCl, $NaHCO_3$, and water, and finally the extract was dried over $MgSO_4$. After filtration, the filtrate was concentrated in vacuo and the mixture purified by flash chromatography on a silica gel column eluting with hexane–ethyl acetate 9:1, to provide a mixture of compounds **7a** and **7b** (0.27 g, 84% yield), which were used without further purification: $^1$H NMR (250 MHz, $CDCl_3$) δ 6.26 (t, $J$ = 2.7 Hz), 5.80 (t, $J$ = 5.9 Hz) in a ratio of 1:4 (total 1 H), 2.53 (s), 2.54 (s) in a ratio of 4:1 (total 3 H), 2.1–1.7 (br m, 10 H), 1.7–1.3 (br m, 10 H), 1.3–1.0 (br m, 4 H); $^{13}$C NMR (62.85 MHz, $CDCl_3$) two sets of signals at δ 215.84, 93.38, 50.73, 42.95, 31.33, 30.89, 27.11, 25.54, 25.08, 18.83 and 215.19, 89.59, 51.89, 40.61, 33.06, 31.66, 27.97, 25.36, 25.26, 18.65 in a ratio of ~4:1; IR (NaCl, neat) 2950 (s), 2867 (s), 1450 (m), 1423 (w), 1228 (s), 1196 (sh), 1056 (s), 966 (m), 915 (w) cm$^{-1}$.

Compounds **7a** and **7b** (0.23 g, 0.74 mmol) in 5.0 mL of dry toluene was added dropwise to a refluxing solution of triphenyltin hydride (1.28 g, 3.6 mmol) in toluene (10.0 mL) over a 20-min period by syringe pump. After the addition was complete, the mixture was heated for an additional 5 h and then cooled to room temperature. The solvent was removed in vacuo and the mixture chromatographed on silica gel eluting with pentane. The title compound (**2**) is the first to elute under these conditions, and 89 mg (58%) of material (95% pure by GC) was obtained: $^1$H NMR (250 MHz, $CDCl_3$) δ 0.7–0.9 (m, 1 H), 1.0–1.35 (m, 6 H), 1.4–2.0 (br m, 19 H); $^{13}$C NMR (62.85 MHz, $CDCl_3$) δ 46.75, 46.19, 38.84, 31.70, 31.69, 30.73, 25.44, 25.40; IR (NaCl, neat) 2948 (s), 2907 (sh), 2864 (s), 1464 (sh), 1450 (m), 1362 (vw), 1331 (w), 1304 (vw), 1256 (vw), 932 (w), 894 (w) cm$^{-1}$. Anal. Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.28; H, 12.42.

**Supplementary Material Available:** Infrared spectra, DSC trace, and wide-angle X-ray diffraction pattern of poly(cyclopentene) and GC and GC–MS analyses of hydro-oligomer mixtures (18 pages). Ordering information is given on any current masthead page.

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## References and Notes

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