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Citation	Autenrieth, Benjamin; Jeong, Hyangsoo; Forrest, William P.; Axtell, Jonathan C.; Ota, Antje et al. "Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of endo-Dicyclopentadiene by Molybdenum and Tungsten Catalysts." <i>Macromolecules</i> 48, no. 8 (April 2015): 2480–2492. © 2015 American Chemical Society
As Published	http://pubs.acs.org/doi/abs/10.1021/acs.macromol.5b00123
Publisher	American Chemical Society (ACS)
Version	Author's final manuscript
Citable link	http://hdl.handle.net/1721.1/108436
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Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of *Endo*-Dicyclopentadiene by Molybdenum and Tungsten Catalysts

by

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Abstract

We report the stereospecific ring-opening metathesis polymerization (ROMP) of *endo*-dicyclopentadiene (DCPD) by various well-defined molybdenum-based and tungsten-based alkylidene initiators. Tungsten MAP (MonoAryloxiide Pyrrolide) initiators with the general formula W(X)(CHCMe₂Ph)(Me₂Pyr)(OAr) (X = arylimido, alkylimido, or oxo; Me₂Pyr = 2,5-dimethylpyrrolide; OAr = an aryloxiide) yield *cis,syndiotactic*-poly(DCPD), while biphenolate alkylidene complexes with the general formula M(NR)(CHCMe₂Ph)(biphen) (M = Mo or W; R = alkyl or aryl, biphen = (e.g.) 3,3'-(*t*-Bu)₂-5,5'-6,6'-(CH₃)₄-1,1'-biphenyl-2,2'-diolate) yield *cis,isotactic*-poly(DCPD). Subtle changes in the initiator can greatly alter the structure of the poly(DCPD)s that are formed. *Cis,syndiotactic* or *cis,isotactic* poly(DCPD)s (made with 50-1000 equiv of DCPD) are accessible within seconds to minutes in dichloromethane at room temperature. No isomerization or cross-linking reactions are observed, and addition of a chain transfer reagent (1-hexene) or the use of THF as a solvent does not decrease the stereospecificity of the polymerizations. *Cis,syndiotactic* and *cis,isotactic* poly(DCPD)s can be distinguished readily from each other by ¹³C NMR spectroscopy. Hydrogenation of each stereoregular poly(DCPD) produces crystalline H-poly(DCPD)s that have melting points between 270 and 290 °C.

INTRODUCTION

Dicyclopentadiene (DCPD) is produced in large quantities as a byproduct of petroleum cracking, which makes DCPD one of the cheapest monomers for ring-opening metathesis polymerization (ROMP) on a large scale.¹ ROMP of DCPD has been studied intensively. Linear poly(DCPD) is formed when the strained norbornene ring is opened selectively, leaving the cyclopentene ring intact.² When a highly electrophilic classical catalyst consisting of a transition metal halide (such as WCl_6) and a main group metal cocatalyst (such as Et_2AlCl) are employed, the poly(DCPD) is heavily crosslinked as a consequence of both ring-opening metathesis and olefin addition reactions between polymer chains.²

Three stereochemical features of poly(DCPD)s prepared through ROMP of only the norbornene ring in DCPD (Figure 1) are relevant. These features (Figure 2) are (i) *cis* or *trans* C=C bonds between polymer units, (ii) a *meso* or *racemic* relationship between two polymer units (excluding the cyclopentene double bond), and (iii) head-to-tail (HT) *versus* head-to-head (HH) or tail-to-tail (TT) orientation of the monomer units as a consequence of the position of the cyclopentene C=C bond.³ (An alternative description for (iii) is whether a neighboring pair of monomer units (a dyad) in the polymer consists of the same enantiomer or different enantiomers. In Figure 2 the choice of where the cyclopentene C=C bond is drawn is arbitrary.) Upon hydrogenation of all C=C bonds, only a *meso* or *racemic* relationship between polymer units remains in the saturated polymer. Because the physical properties of a polymer depend upon its microstructure, it is desirable to form a wholly *isotactic* or a wholly *syndiotactic* hydrocarbon polymer as an end product. The most feasible approach is to develop catalysts that lead selectively to one of the two *isotactic* structures (*cis* or *trans*), or one of the two *syndiotactic* structures (*cis* or *trans*).

Well-defined Mo, W and Ru alkylidene complexes have been developed in the last 20-25 years that are capable of controlling the ROMP process with ever-increasing precision.⁴ An approach that led to formation of *cis, isotactic* polymers through ROMP was discovered in 1993.⁵ This approach employs Mo and W imido alkylidene catalysts that contain a chiral, but racemic,

C_2 -symmetric biphenolate or binaphtholate ligand. A biphenolate or binaphtholate ligand can force the monomer to add to the same enantiotopic face of the $M=C$ bond in each step (enantiomorphic site control), much as found in catalysts for the *isotactic* polymerization of propylene.⁶ A polymer with *cis* linkages is formed if the monomer adds to the *syn* alkylidene isomer to give an all *cis* metallacyclobutane intermediate.^{5,7} If enantiomorphic site control fails, a mixed tacticity, and/or a mixture of *cis* and *trans* linkages will result. It is unlikely that a perfect *syndiotactic* polymer will be formed from a catalyst that contains a racemic chiral ligand. It has become possible recently to prepare *cis,syndiotactic* polymers employing catalysts *whose chirality at the metal inverts with each addition of monomer*. As a consequence of inversion at the metal the monomer will add alternately to one $M=C$ face and then the other.^{8,9} Therefore, we can now anticipate the synthesis of both *cis,isotactic* and *cis,syndiotactic* polymers from a single monomer as well as the synthesis of *isotactic* and *syndiotactic* hydrocarbon polymers from them upon hydrogenation of all double bonds.^{9a}

During approximately the last decade Hayano and coworkers have endeavored to polymerize *endo*-dicyclopentadiene stereoselectively with Mo and W initiators in which the metathetically active alkylidene complex is generated (or complexes are generated) *in situ* from a $M(VI)$ oxo or imido precursor and some alkylating agent.^{3,10} The object ultimately is to prepare a thermally-stable and oxygen-stable hydrogenated poly(DCPD) (H-poly(DCPD)) that has a single tacticity. Excellent progress toward the synthesis of pure *isotactic*-H-poly(DCPD) and pure *syndiotactic*-H-poly(DCPD) has been made, although the ultimate goal of preparing essentially 100% *isotactic*-H-poly(DCPD) or *syndiotactic*-H-poly(DCPD) has not yet been reached.

The most feasible approach to formation of *isotactic*-H-poly(DCPD) and *syndiotactic*-H-poly(DCPD) is to prepare *cis,isotactic*-poly(DCPD) with tungsten or molybdenum biphenolate complexes, which operate through enantiomorphic site control, and *cis,syndiotactic*-poly(DCPD) with MAP (MonoAryloxide Pyrrolide) catalysts, which operate through stereogenic metal control.^{9a} We report here the results of our evaluations of a significant number of catalysts in each of these categories for the *cis,isospecific* and *cis,syndiospecific* ROMP of DCPD.

RESULTS AND DISCUSSION

The types of complexes that have been evaluated are shown in Figures 3 and 5. All initiators in Figure 3 (**2-16**) are MAP complexes. All those in Figure 5 are either biphenolate imido alkylidene complexes (**17-22**) or bisaryloxide tungsten oxo alkylidene complexes (**23-26**) in which the aryloxide is especially bulky. Bisaryloxide tungsten oxo alkylidene complexes have been prepared only recently^{9b,11} and any control that would be observed would likely be chain end control. The reference initiator is Mo(NAr)(CHCMe₂Ph)(O-*t*-Bu)₂ (**1**; Ar = 2,6-*i*-Pr₂C₆H₃), which has been observed to give both *cis* and *trans* atactic polymers in many circumstances, although *trans,syndiotactic* polymers sometimes can be prepared relatively selectively through a chain end control process.^{8c,9a}

ROMP to give poly(DCPD)s

All initiators consume up to 200 equivalents of monomer at a high rate (see Table 1). When polymerizations were conducted in the presence of a chain transfer reagent (1-hexene, *vide infra*), >5000 equivalents of DCPD could be polymerized without altering the stereoselectivity of the process. All reactions were performed at room temperature in dichloromethane. Integration of the olefinic proton region *versus* the aliphatic proton region in the ¹H NMR spectrum of the resulting polymers was found to be 4:8 in all cases (for example, see Figure S1 in the SI) consistent with a ROMP process that involves the norbornene ring only. The chemical shifts for the methine carbon resonances C2 and C5 (Figure 1) in a *cis* configured polymer are separated from those in a *trans* configured polymer. The percentage of *cis* double bonds consequently was estimated from ¹³C NMR spectra through integration of the resonances for the methine carbons C2/C5 in *cis* and *trans* configured segments (*vide infra*, Figures 4a and S2, SI). The tacticities for polymers having an all *cis* configuration can be determined through examination of the ¹³C NMR spectra of the poly(DCPD)s. When a biphenolate catalyst yields a regular *cis* structure, that structure is most likely *cis,isotactic*, as described below, especially if a regular and therefore most likely a *cis,syndiotactic* polymer is formed with a MAP catalyst.

Syndiotactic poly(DCPD)s

Molybdenum-based and tungsten-based MAP catalysts that were screened for the stereospecific ROMP of DCPD (**2** - **16**) are shown in Figure 3. Poly(DCPD) prepared from Mo(NAr)(CHCMe₂Ph)(O-*t*-Bu)₂ (**1**; Ar = 2,6-*i*-Pr₂C₆H₃) was employed as a reference with which to compare the more tactic polymers generated by other initiators. Poly(DCPD)¹ (prepared employing **1**) has 80% *trans* double bonds in the backbone and is soluble in dichloromethane at room temperature. The ¹³C NMR spectrum of poly(DCPD)¹ shown in Figure 4a is typical for irregular poly(DCPD).^{2c} (For full spectra see Figures S1 and S2 in the SI). The methine carbon resonances C2 and C5 are found at 45.87 and 47.13 ppm in a *trans* structure and at 41.25 and 42.43 ppm in a *cis* structure.

Initiators **2** - **6** are all tungsten-based imido alkylidene MAP species. Complex **2** should form *cis,syndiotactic*-poly(DCPD)² through stereogenic metal control as a consequence of the presence of the "small" *tert*-butylimido group in combination with a bulky HMTO ligand and inversion of the configuration at the metal with each step in the polymerization. The ¹³C NMR spectrum of poly(DCPD)², which is relatively simple (Figure 4b, Figure S3, SI), allows us to conclude that it is a >98% *cis*, >98% *syndiotactic* polymer; no carbon resonances for *trans* C=C bonds are observed in the ¹³C NMR spectrum. Two methine carbon (C3) resonances have chemical shifts of 45.00 and 44.84 ppm, while two C4 resonances are found more downfield at 55.06 and 54.94 ppm.^{8,12} In theory twenty separate carbon resonances could be observed for dyads that contain the same enantiomer or different enantiomers; eight separate resonances of approximately equal intensity can be observed for C2-C5 in Figure 5b, while only five of the possible eight olefinic carbon resonances can be observed in a ratio of 1:1:3:1:2. No C=C bond isomerization or cross-linking through the cyclopentene double bond was detected upon stirring the reaction mixture for more than one hour after reaching full conversion, but before quenching with benzaldehyde. These and other results discussed below are summarized in Table 1.

MAP initiator **3** yields poly(DCPD)³ smoothly and rapidly. The ¹³C NMR spectrum of poly(DCPD)³ (Figure S4, SI) is identical to that of poly(DCPD)². It is somewhat surprising that **3**

yields a *cis,syndiotactic* polymer because the 2,6-diisopropylphenylimido (NAr) ligand is so much more sterically demanding than a *t*-butylimido ligand.

Complex **4**, an unsubstituted metallacyclobutane complex that contains the bulky HIPTO ligand (HIPTO = O-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃), produces a polymer that contains ~80% *cis* double bonds in its backbone. A 70% *syndiotactic* polymer was formed upon hydrogenation (*vide infra*). Catalyst **4** is the slowest of all initiators shown in Figure 3; 60 minutes are required to fully polymerize 100 equivalents of monomer. The low rates and the degradation of *cis* selectivity can both be attributed to the increased steric bulk of the HIPTO ligand relative to the HMTO ligand. This metallacyclobutane complex also only slowly loses ethylene to yield a methylenide,²¹ so the rate of initiation may be relatively slow compared to the rate of propagation.

Complexes **5** and **6** were chosen in order to evaluate the effect of more electron-withdrawing imido or phenoxide ligands. Catalyst **5a** yields a polymer that is ~90% *cis,syndiotactic*. The reaction is fast but it does not proceed in as controlled a manner as with initiators **2** and **3**; some *trans* double bonds are formed. Complex **5b** yields poly(DCPD) that has 85% *cis* double bonds in its backbone, so dimethylpyrrolide (in **5b**) and pyrrolide itself (in **5a**) yield initiators that are approximately the same in terms of their *cis* selectivity. These results suggest to us that the electron-withdrawing character of the 2,4,6-trichlorophenyl imido ligand is responsible for the decreased selectivity of catalysts **5a** and **5b**. Catalyst **6**, which also contains a decafluoroterphenoxide (DFTO) ligand in place of the HMTO ligand, is even less tactoselective; poly(DCPD)⁶ contains all *cis* C=C bonds, but the *meso:racemo* ratio is 35:65. The polymerization proceeds most rapidly with initiator **6**, which we attribute to the presence of the electron-withdrawing imido and DFTO ligands, followed by **2**, **3**, **5a**, and **5b**.

Tungsten complexes **7–11** are all oxo compounds. Both initiators **7** and **8** rapidly yield 100% *cis* poly(DCPD). No post polymerization changes are observed even when addition of benzaldehyde (as a quenching agent) is delayed by 3 h. The ¹³C NMR spectrum of poly(DCPD)⁷ is virtually identical to spectra of poly(DCPD)² and poly(DCPD)³, namely essentially 100% *cis*

and 100% *syndiotactic* (Figure S5, SI). The PPh_2Me ligand is known to dissociate readily to give the four-coordinate 14 electron species. Less is known about the lability of acetonitrile on the polymerization time scale and the potential reactivity of the 16 electron acetonitrile adduct. At room temperature, poly(DCPD)⁸ was found to be 100% *cis*, but ~75% *syndiotactic* and ~25% *isotactic* (Figure 4c, Figure S6, SI); resonances characteristic of a *cis,isotactic* dyad structure appear at 45.42 and 45.31 ppm for C3 and 55.57 and 55.48 ppm for C4. The ROMP of 2,3-dicarbomethoxynorbornadiene initiated by $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{ODFT})(\text{MeCN})$ has also been shown to produce *cis*, but atactic polymer, as opposed to *cis,syndiotactic* polymer from $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{DFTO})$.¹¹ ROMP of DCPD initiated by **8** at 30 °C is more *syndioselective* (83%), but at 50 °C a 100% *cis,atactic* polymer was formed (*meso:racemo* = 1:1). We attribute the increased stereoselectivity at 30 °C (relative to that at 22 °C) to a more ready loss of acetonitrile at 30 °C, but at 50 °C the *syndioselectivity* is lost. For comparison, complex **2** was employed as an initiator at 50 °C. Again, the 100% *cis* polymer was found to be atactic. There are several possible reasons for a loss of selectivity, but whatever the reason in any specific case, it should be noted that temperature is likely to be an important variable, especially in exothermic polymerizations of norbornenes on a large scale. In general, temperature effects employing selective polymerization with well-defined catalysts, and what leads to the observed effects, have not been explored in literature reports. $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{ODFT})(\text{PMePh}_2)$ (**9**) is a highly active catalyst, polymerizing 100 equivalents of DCPD within 30 seconds. However, the resulting polymer still has a *cis,syndiotactic* structure (Figure S7, SI). Complex **9** consequently provides the advantage of increasing the reaction rate while preserving the desired stereoselectivity in the ROMP of DCPD.

Complexes **10** and **11** were chosen because the aryloxy ligand in each is less exotic than the terphenoxides described so far. Complex **10** contains the 2,3,5,6-tetraphenylphenoxide (TPPO) ligand, which is readily prepared in a one pot reaction from relatively inexpensive starting materials. Even though TPPO is less sterically demanding than HMTO, **10** provides *cis,syndiotactic* poly(DCPD) at rates comparable to those observed for **2** and **7**. Again, no

secondary isomerization or crosslinking reactions were observed (Figure S8, SI). Complex **11** contains the commercially available 2,6-diphenylphenoxide (DPPO) ligand. A *cis*, but less tactic polymer is formed in this case (Figure S9, SI).

The molybdenum-based MAP complexes **12** - **16** were chosen because **12** is the Mo analog of **2**, **15** is the Mo analog of **3**, and the three permanent ligands on **16** are analogous to those on **4**. Interestingly, although in all cases the reaction rates were higher employing the molybdenum catalysts than tungsten-based analogs, none of the molybdenum-based initiators provides a polymer with a single structure, or even an all *cis* polymer (Table 1). Poly(DCPD)¹² contains 68% *cis* double bonds, while poly(DCPD)¹³ contains 62% *cis* double bonds. Hydrogenation of both polymers yielded atactic polymers with *racemo:meso* ratios of ~1:1. With initiators **12** and **13** at 0°C, 100 equivalents of monomer are still consumed within seconds and again atactic polymers are formed. At -80°C the polymerization was complete only after 1h, and atactic polymers again were formed. It was not possible to entirely dissolve the polymer formed from **14**, perhaps as a consequence of some (we propose metathesis-based) cross-linking. Initiator **15** showed the highest stereoselectivity in the ROMP of DCPD. Initiator **15** was less reactive than **12** or **13**, most probably as a consequence of the increased steric bulk of the 2,6-diisopropylphenylimido ligand. The resulting poly(DCPD)¹⁵ has 80% *cis* double bonds and, upon hydrogenation, was found to yield a 90% *syndiotactic* poly(DCPD) (Figure S10, SI). Initiator **16** features the bulky HIPTO ligand. At room temperature **16** produces an atactic polymer that has only 60% *cis* double bonds in its backbone.

At this point it can be stated that among the catalysts shown in Figure 3, tungsten seems to be more successful for the *cis,syndioselective* ROMP of *endo*-dicyclopentadiene than molybdenum, especially initiators **2**, **3**, **7**, **9**, and **10**. Electron-withdrawing aryloxides such as DFTO appear to increase the reactivity of a W-based MAP catalyst without decreasing the desired stereoselectivity, at least in the case of initiator **9**. Coordination of acetonitrile, as in initiator **8**, degrades the tactoselectivity. These findings once more illustrate the importance of

employing well-defined catalysts whose structures and modes of behavior are known in order to determine the origin of stereospecificity and point the way to further research and improvement.

One final point is that the neighboring monomer units (dyads) in poly(DCPD) can be created from the same enantiomer of the monomer (AA or BB pairs) or opposite enantiomers (AB pairs). If all carbon resonances in the ^{13}C NMR spectrum of *cis,syndiotactic*-poly(DCPD) that contains a 1:1 random collection of AA/BB and AB pairs were resolved, eight olefinic and twelve aliphatic resonances potentially could be observed. In Figure 4b ten of the theoretical twelve aliphatic carbon atom resonances are observable, while only five olefinic carbon resonances are observed. Although a *cis,syndiotactic*-poly(DCPD) in which the enantiomers have been incorporated alternately (in an ...ABABAB... sequence) cannot be eliminated as a possibility on the basis of these data, we believe that structure to be unlikely. It also is not possible to carry out a kinetic resolution of racemic DCPD (e.g., to give ...AAAAA... polymer) because the initiator is not enantiomerically pure.

Isotactic poly(DCPD)s

The Mo and W biphenolate complexes and W-based bisaryloxides that were employed as initiators are shown in Figure 5. Complexes **17** - **22** feature biphenolates with *t*-butyl groups in the 3 and 3' positions, a type of ligand that was developed and employed for ROMP over 20 years ago.⁵ The incoming monomer is forced to approach one face of the M=C bond repeatedly as a consequence of steric interactions and all substituents in the intermediate metallacyclobutane are forced to point towards the axial imido or oxo ligand in the presumed intermediate TBP metallacyclobutane complex. Ideally the resulting polymer therefore should be *cis,isotactic*. The complexes differ in the size of their imido ligands as well as in the electronic properties of the respective biphenolates. Only chain end control should be possible with initiators **23** - **26**.

Initiators **17** - **22** all polymerize 200 equivalents of DCPD in less than one minute. The poly(DCPD)s prepared employing initiators **17** - **22** precipitate out of the reaction mixture as they are formed and the samples can be redissolved in chloroform only at elevated temperatures. *Cis,syndiotactic* polymers are soluble at room temperature. Apparently *cis,isotactic*-poly(DCPD)

is significantly less soluble than *cis,syndiotactic*-poly(DCPD), as has also been observed by Hayano.¹⁰

Complexes **20** and **21** bearing an electron withdrawing 3,3'-(*t*-Bu)₂-5,5'-(CF₃)₂-6,6'-(CH₃)₂-1,1'-biphenyl-2,2'-diolate (biphenCF₃) were prepared from the corresponding Mo bistriflate precursors in THF and were isolated as THF adducts, while **19** was isolated as a four-coordinate, THF-free complex.²⁵ Four-coordinate complexes **17**, **18**, and **22** were prepared from the corresponding bispyrrolides in benzene. Generally, polymerization of DCPD proceeds more slowly for the THF adducts **20** and **21**, probably because THF blocks coordination of the substrate to some degree (see later). Nevertheless, the reactions are complete within ~1 minute. Initiators **17**, **18**, **19**, and **22** yield *cis*, isotactic polymers that could be redissolved in C₂D₂Cl₄ only at 140°C. The polymer derived from **20**, which features biphenCF₃ and 2,6-dimethylphenyl ligands, possesses 90% *cis* double bonds in its backbone and is >95% *isotactic* (Figure S12, SI). Poly(DCPD)²⁰ could be redissolved in CDCl₃ readily at 55°C. The ¹³C NMR spectra of polymers that contain 50 monomer units (on average ideally) and those made up of 200 monomer units (on average ideally) are virtually identical. Complex **21** bears a small adamantylimido substituent and an electron-withdrawing biphenolate and gives poly(DCPD)²¹ that contains 15% *trans* double bonds in its backbone. As mentioned above, the all *cis* polymers prepared from **17**, **18**, **19**, and **22** were soluble only at 140°C in 1,1,2,2-tetrachloroethane-d₂ as a consequence of their high isotactic content. High temperature ¹³C NMR measurements revealed that Mo complex **17** and its tungsten analog **22** yielded pure *cis,isotactic*-poly(DCPD). The chemical shifts for the methine carbons C3 and C4 exactly match the ones assigned to a *meso* dyad in poly(DCPD)⁸. Therefore we are confident that the chemical shifts for the methine carbons C3 (45.44 and 45.33 ppm) and C4 (55.56 and 55.48 ppm) are characteristic of a *cis,isotactic* microstructure (Figure S14, SI). Both complexes feature 2,6-dimethylphenylimido and 3,3'-(*t*-Bu)₂-5,5'-6,6'-(CH₃)₄-1,1'-biphenyl-2,2'-diolate ligands. The polymer derived from complex **18**, bearing the more bulky 2,6-diisopropylphenylimido ligand, is all *cis*, but only 90% *isotactic* (Figure S15, SI). Catalyst **19**, which features an adamantyl imido ligand, gave poly(DCPD)¹⁹ that is essentially 100% *cis*,

but only 75% *isotactic*. Both **18** and **19** contain the 3,3',5,5'-(*t*-Bu)₄-6,6'-(CH₃)₂-1,1'-biphenyl-2,2'-diolate ligand; the two *t*-butyl groups in the 5 and 5' positions obviously have some positive effect on the *cis*-selectivity of **18** and **19**, but a negative effect on isoselectivity.

We did not expect the W-based bisaryloxide complexes **23** – **26** (Figure 5) to be successful for forming *cis, isotactic*-poly(DCPD) because only chain end control is possible in achiral bisaryloxides. Complexes **23**, **24**, **25**, and **26a** all produce poly(DCPD)s that are essentially 100% *cis*. The polymerization of DCPD with W(O)(CHCMe₂Ph)(OHMT)₂ (**23**) was relatively slow, with only 50 equivalents of DCPD being converted in 30 minutes to give a polymer that is 70% *syndiotactic*. In contrast, W(NC₆F₅)(CHCMe₂Ph)(ODFT)₂ (**25**) polymerizes 200 equivalents of DCPD in ~30 seconds. Figure S16 (SI) shows the ¹³C NMR spectrum of *cis*, 70% *isotactic* poly(DCPD)²⁵. W(O)(CHCMe₂Ph)(OTPP)₂(PMePh₂) (**24**) is less reactive than **25** but also yields *cis*, 70% *isotactic* poly(DCPD)²⁵. Poly(DCPD)^{26a} generated from W(N-2,4,6-Cl₃C₆H₂)(CHCMe₃)[O-2,6-(CHPh₂)₂-3-MeC₆H₂]₂ (**26a**) has essentially the same structure as the poly(DCPD)s derived from **25** and **24** (Figure S17, SI). Complex **26b** differs from **26a** in that its phenylimido ligand contains bromides in the 2, 4, and 6 positions. Polymerization by **26b** is faster than polymerization by **26a**, but the resulting polymer contains 19% *trans* double bonds in its backbone and the *meso:racemo* ratio is reduced to 63:37. Reduction of the *cis* selectivity might be attributed to the presence of a more bulky imido ligand in **26b** compared to **26a**, because all substituents are less likely to point toward a more sterically demanding imido ligand in the metallacyclobutane intermediate.

As discussed in the section above devoted to *cis, syndiotactic*-poly(DCPD), there is no bias toward a *cis, isotactic*-poly(DCPD) in which enantiomer A and enantiomer B are alternately incorporated in an ...ABABAB... fashion, nor is there any clear rationale how such a structure would be formed with a bisaryloxide initiator, or even a biphenolate initiator. Six olefinic carbon resonances in a ratio of 1:1:1:1:2:2 (out of potentially eight) are more visible in Figure 4d than in Figure 4b (see also Figures S13, S14, S15, SI).

In summary, for the collection of complexes shown in Figure 5, Mo or W biphenolate alkylidene complexes appear to be the most reliable for preparing *cis, isotactic*-poly(DCPD). Tungsten-based complexes **23**, **24**, **25** and **26a** are 100% *cis* selective, but do not provide any tacticity control.

THF or toluene as solvents

THF and toluene were explored briefly as solvents for polymerizations with initiators **2**, **7**, **9**, **17**, **20(hex)**, and **22**. The monomer concentration was 2 wt% in all experiments and 100 equivalents of DCPD were polymerized. In no case did the selectivities listed in Table 1 change when the polymer was prepared in THF or toluene, although in THF the polymerization was noticeably slower (2-5 minutes) employing **2**, **7**, or **9**, roughly double the time required when CH₂Cl₂ was the solvent. Polymerizations initiated by **17**, **20(hex)**, and **22** were all complete within one minute regardless of the solvent chosen, and *cis, isotactic*-poly(DCPD)s precipitated out of the reaction mixture. When **2**, **7**, and **9** were used in toluene, a gel of relatively insoluble *cis, syndiotactic*-poly(DCPD) formed during polymerization.

1-Hexene as a Chain Transfer Agent

A terminal olefin such as 1-hexene is a known chain transfer agent (CTA) for ROMP reactions that is useful for limiting the molecular weights of the monomer produced.^{2c,13} Some of the 1-hexene is likely to be homometathesized to ethylene and 5-pentenenes in the process. We became interested first, in whether the high stereoselectivities we have observed for poly(DCPD)s (Table 1) would be compromised in the presence of 1-hexene, and second, in how low a catalyst loading could be reached. Initial screening experiments were performed at room temperature in dichloromethane with 1000 equivalents of DCPD and 50 equivalents of 1-hexene relative to initiator. The complexes that were examined represent a selection of W-based MAP complexes (**2**, **7**, **9**) or Mo- or W-based biphenolate complexes (**17**, **20**, **22**). All reactions were performed at room temperature. All initiators chosen, with the exception of **20**, were stereoselective for formation of *cis, syndiotactic* or *cis, isotactic* polymers, respectively. When

using 1-hexene as a CTA, ethylene is likely to be formed through metathesis homocoupling, and therefore methylenes and (for tungsten) relatively stable unsubstituted metallacyclobutanes.

All ^{13}C NMR spectra of the resulting polymers are virtually identical for a given regular polymer (*cis,syndio* or *cis,iso*) with the exception of observable hexenyl end groups. For example, initiator **9** with 1000 equivalents of DCPD and 5 mol% (50 equiv) 1-hexene yielded a polymer whose resonances for the pentylidene end group could be observed in the proton NMR spectrum; integration of the methyl group in the pentylidene end group showed that on the average a 37 mer was formed, *assuming* that a pentylidene end group is present on each polymer chain. If the 1-hexene had been completely consumed to yield polymers with methylenes and pentylidene end caps over the course of the polymerization the average polymer would be a 20 mer. Therefore it is clear that 1-hexene is a relatively good chain transfer agent under the conditions employed, but that it is not completely consumed in that role. A similar conclusion was reached by Hayano.^{3b}

Initiators **17** and **20** produced *cis,isotactic*-poly(DCPD) from up to 50000 equivalents of DCPD in the presence of 1-hexene. No resonances for the end groups are visible in these polymers. Interestingly, initiator **20**, which was found to yield 90% *cis*, 95% *isotactic* poly(DCPD) in the absence of 1-hexene (*vide supra* and Table 1), instead formed pure *cis,isotactic*-poly(DCPD) in the presence of 5 mol% 1-hexene (Figure 4d, Figure S13, SI). At this time we have no explanation as to why *cis,isotactic*-poly(DCPD) is formed in the presence of 5 mol% 1-hexene, but not on the absence of 1-hexene.

We conclude that addition of 1-hexene does not negatively affect the stereoselectivity of DCPD polymerization by W MAP and Mo/W biphenolate alkylidenes, and that addition of 1-hexene actually improves the ability of **20** to form *cis,isotactic*-poly(DCPD) selectively. No significant isomerization or cross-linking reactions were observed under the conditions employed.

Studies concerning k_p/k_t

One of the important issues in polymerizations is the ratio of the rate constant for

propagation (k_p) to that for initiation (k_i). A method for determining k_p/k_i values in ROMP, if the k_p/k_i value is within an appropriate range, was published in 1990.¹⁴ This method assumes that a single initiating and a single propagating species are being observed. We now know that this assumption is not valid because two alkylidene isomers of the initiator (*syn* and *anti*) potentially are interconverting with one another and two alkylidene isomers of the propagating species potentially are interconverting with one another.¹⁵ However, even though it may not be known which alkylidene isomer is the initiator and which isomer is the propagating species, the overall rate constants for initiation versus propagation nevertheless can still be measured.

Values of k_p/k_i for reactions of DCPD (8 equivalents) in CH_2Cl_2 at 22°C with several initiators are listed in Table 3. The samples were examined by ^1H NMR spectroscopy in order to quantify the alkylidene resonance that is visible for the initiator *versus* those for propagating alkylidenes. For $\text{W}(\text{N-}t\text{-Bu})(\text{CHCMe}_3)(\text{pyr})(\text{OHMT})$ (**2**) the original alkylidene resonance is almost gone and multiple new resonances are visible in the ^1H NMR spectrum (Figure S39, SI). A k_p/k_i value of ~ 1 was found, and the poly(DCPD) was confirmed to be *cis,syndiotactic*, as found in large scale polymerizations. In contrast, the majority of $\text{Mo}(\text{N-Ad})(\text{CHCMe}_3)(\text{pyr})(\text{OHMT})$ (**12**) (Figure S40, SI) and $\text{Mo}(\text{N-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{pyr})(\text{OHMT})$ (**13**) did not react with DCPD before DCPD was consumed; k_p/k_i could be calculated to be 13-14. The relatively high k_p/k_i values observed for $\text{Mo}(\text{N-2,6-Me}_2\text{Ph})(\text{CHCMe}_2\text{Ph})(\text{rac-biphen})$ (**7**) and $\text{Mo}(\text{N-2,6-Me}_2\text{Ph})(\text{CHCMe}_2\text{Ph})(\text{THF})(\text{rac-biphenCF}_3)$ (**20**) help explain why no hexenyl end groups are visible in the NMR spectra of the resulting polymers made in large scale polymerizations with these initiators.

Preparation of Hydrogenated H-poly(DCPD)s

Hydrogenation of a wide range of poly(cycloolefins), including poly(DCPD), has been employed widely as a means of eliminating the long term instability of polymers in the air.^{2c,3,16} The physical properties of a hydrogenated poly(cycloolefin) also often differs dramatically from the properties of its unsaturated precursor.

Poly(DCPD)s were hydrogenated with diimine generated *in situ* from *p*-toluenesulfonyl hydrazide (*p*-TosylNHNH₂, Figure 6). In order to keep the polymers in solution, hydrogenation reactions were performed in chloroform in a pressure tube at 130 °C employing four equivalents of *p*-TosylNHNH₂ per DCPD.

Atactic H-poly(DCPD) formed through hydrogenation of poly(DCPD)¹ is soluble in chloroform at room temperature. Its full NMR spectrum (in CDCl₃) is shown in the Supporting Information (Figures S18 and S19). A high degree of saturation is proven by the absence of olefinic proton resonances in ¹H NMR spectra and olefinic carbon resonances in ¹³C NMR spectra. As expected, two resonances each for C2/5 and C8/10 are observed in the ¹³C NMR spectrum (Figure 7a) as a consequence of the presence of both *meso* and *racemo* dyads. As described in the literature,^{2c,3,12} the resonance for C2/C5 at 42.94 ppm can be assigned to a *syndiotactic* structure (Figure 7b) and the resonance at 42.89 ppm to an *isotactic* structure (Figure 7c). The *atactic* polymers prepared from Mo MAP complexes **12** and **13** are still soluble after hydrogenation. Both polymers possess *meso:racemo* ratios of roughly 1:1 and the chemical shifts are the same (within experimental error) as for the H-poly(DCPD) derived from **1**. Generally, the more regular the poly(DCPD), the less soluble (and more crystalline) is the resulting H-poly(DCPD). Initiator **4**, which features the bulky HIPTO ligand, was found to give a 80% *cis*, 70% *syndiotactic* poly(DCPD), and H-poly(DCPD)⁴ is soluble in CHCl₃ upon heating to 55°C (for the ¹³C NMR see Figure S20, SI). Both the unsaturated and hydrogenated version of the all *cis*, 70% *isotactic* polymer generated from **25** proved to be less soluble than its 70% *syndiotactic* analog. The hydrogenated polymers derived from **2**, **3**, **7**, **9**, **10** (all *syndiotactic*), **17**, **20(hex)**, and **22** (all *isotactic*) are entirely insoluble in common organic solvents at room temperature. The solubility generally increases with decreasing molecular weight, but even for the H-poly(DCPD)s that theoretically contain 50 monomer units, a temperature of 100°C is necessary to obtain good quality ¹H NMR spectra. In order to investigate the respective tacticities of these relatively insoluble polymers, ¹³C NMR spectra had to be recorded in C₂D₂Cl₄ at 140°C. Because the chemical shifts observed in C₂D₂Cl₄ at elevated temperatures differ from those recorded in

chloroform at room temperature, a ^{13}C NMR spectrum of atactic H-poly(DCPD) derived by **12** also was recorded as a reference at 140°C (Figure 7a). In addition to two resonances for C8/C10, the methine carbons C2/C5 also yield two resonances as a consequence of tacticity differences at the dyad level. The resonance for C7 is split into resonances for rr, rm/mr, and mm structures at the triad level in Figure 7a.

The ^{13}C NMR spectra of H-poly(DCPD)s derived from **2**, **3**, **7**, **9**, and **10** all show six resonances. The chemical shift of 42.95 ppm for the methine carbons C2/C5 matches the chemical shift that was assigned to a *syndiotactic* dyad in the atactic reference polymer (Figure 7b, Figure S21, SI). Carbons C2/C5 in the H-polymers derived by biphenolate catalysts **17**, **20(hex)** and **22** have a chemical shift of 42.89 ppm, which was ascribed to an *isotactic* relationship in the atactic reference polymer (Figure 7c, Figure S22, SI). All tactic poly(DCPD)s and H-poly(DCPD)s that are derived from the different biphenolate catalysts show exactly the same chemical shifts, and all tactic poly(DCPD)s derived from the MAP species show exactly the same chemical shifts. On the basis of these findings, the chemical shifts of pure *cis,syndiotactic* and pure *cis,isotactic* poly(DCPD)s and H-poly(DCPD)s can now all be assigned with confidence (see Experimental section).

Thermal behavior of *syndiotactic* and *isotactic* H-poly(DCPD)s

The thermal properties of hydrogenated poly(DCPD)s that are highly *syndiotactic* or *isotactic* have been investigated in detail in the literature.¹⁰ Although atactic H-poly(DCPD) is amorphous, H-poly(DCPD)s that contain predominantly one microstructure are crystalline polymers with melting points above 270°C.^{3,10} We carried out a preliminary investigation of the thermal behavior of the tactic H-poly(DCPD)s prepared here through differential scanning calorimetry (DSC) and wide angle x-ray diffraction (WAXRD). The *syndiotactic* H-poly(DCPD)s that were examined were derived from initiators **2** and **9(hex)** and *isotactic* H-poly(DCPD)s from **17** and **20(hex)**. Polymers were prepared with **2** and **17** and 50 or 100 equivalents of DCPD, or with **9(hex)** and **20(hex)** and 1000 equivalents of DCPD in the presence of 5 mol% 1-hexene. The most important results are summarized in Table 4.

As shown in Figure 8, the DSC traces of the *syndiotactic*-H-poly(DCPD) made of 50 equivalents of DCPD show large endothermic peaks (melting) at temperatures near and above 270°C and large exothermic peaks (due to crystallization) at temperatures at around 200°C. This behavior is found for all *syndiotactic*-H-poly(DCPD)s and confirms that these polymers are highly crystalline. (All data retrieved from DSC measurements can be found in the Supporting Information.) As is generally observed for polymers without heat hysteresis, the melting enthalpy detected during the first scan is larger than enthalpies observed in the following scans and melting is found in the first scan at slightly higher temperatures than in subsequent scans. For *syndiotactic*-H-poly(DCPD)s the melting enthalpy during the first heating was ~55 J/g for all polymers (Table 5); in the following cycles a value of ~26 J/g was detected. A melting enthalpy of ~50 J/g was measured for *isotactic*-H-poly(DCPD) during the first heating cycle. A common explanation is that crystallization in the polymer melt leads to lower crystallinities than crystallization from solutions. Melting and recrystallization are highly reproducible for *syndiotactic* H-poly(DCPD), i.e., the temperatures for each differ by only ~2 °C in the second and tenth heating/cooling cycles.

Isotactic-H-poly(DCPD)s also melt at high temperatures and are crystalline, but recrystallization from the melt is relatively slow;³ results can be found in the SI, but are not discussed here in detail. The melting point of *isotactic*-H-poly(DCPD) is located roughly 20°C above that observed for the *syndiotactic* material, but melting is most pronounced in the first heating cycle and the peaks broaden significantly during the consecutive cycles. This same observation has been reported and explained in terms of differences in crystal structures between *syndio*- and *isotactic*-H-poly(DCPD)s.^{3,10} All H-poly(DCPD)s show small glass transitions at 97 °C regardless of their microstructures or molecular weights (Table 4); similar glass transitions are observable even in hydrogenated atactic poly(DCPD)s.^{3,10} The melting transitions in the first heating cycle are located at around 274 °C for all *syndiotactic*-H-poly(DCPD)s. From the second cycle onwards samples melted at around 270 °C. However, polymers with longer chains crystallize at lower temperatures than those with shorter chains. This result is to be expected

because it is more difficult for longer polymers to arrange in a highly structured manner than for shorter polymers. Thus, *syndiotactic*-H-poly(DCPD) with the lowest molecular weight (made in the absence of 1-hexene) recrystallizes at 209 °C while the sample with the highest molecular weight recrystallizes at 168 °C in a scan with the same speed (Table 4). *Syndiotactic*-H-poly(DCPD) prepared by catalyst **9** in the presence of 5 mol% 1-hexene (**9(hex)**) showed a T_c of 230 °C (Table 4 and Figure S29, SI). In addition, the melting temperature and enthalpy in the first heating cycle do not differ significantly from those in later cycles. We have found that *isotactic*-poly(DCPD), whether prepared in the absence or presence of 1-hexene, shows a melting point at around 290°C, which is consistent with its high crystallinity and poor solubility.

Figure 9 shows the WAX diffraction patterns for *syndiotactic*-H-poly(DCPD) and *isotactic*-H-poly(DCPD) obtained from solution. The diffraction pattern of the syndiotactic polymer clearly differs significantly from the diffraction pattern for the isotactic polymer. Both tacticities produce highly crystalline polymers with degrees of crystallinities (w_c) that far exceed those of the most common poly(hydrocarbon)s and, in fact, are comparable to those reported for high density polyethylene.¹⁷ The crystallinity (w_c) was found to be 0.83 for the *syndiotactic*-H-poly(DCPD) formed through polymerization of 50 equivalents DCPD by catalyst **2**. It is worth mentioning that for the *syndiotactic*-H-poly(DCPD) prepared from initiator **9** in the presence of 5 mol% 1-hexene (**9(hex)**) the crystallinity was also high ($w_c = 0.82$). The presence of a small percentage of pentylidene end groups do not seem to impact the crystallinity of *syndiotactic*-H-poly(DCPD) negatively. *Syndiotactic*-H-poly(DCPD) made from 100 equivalents of DCPD instead of 50 resulted in a w_c of 0.80. Even when 200 equivalents of DCPD were polymerized by **2**, the resulting *syndiotactic*-H-poly(DCPD) was found to have a crystallinity of 0.83. In case of pure *isotactic*-H-poly(DCPD) prepared from **17**, a degree of crystallinity of 0.68 was detected for the polymer prepared of 50 equivalents DCPD. Doubling the amount of monomer (to 100) results in a hydrogenated polymer that has a crystallinity of 0.55. Consistently, the *isotactic*-H-poly(DCPD) generated from initiator **20** in the presence of 5 mol% 1-hexene (**20(hex)**) possesses

a crystallinity of 0.74 (Figure 9). A much more thorough investigation of the dependence of crystallinity on a polymer with a *measured* molecular weight will be desirable in future studies.

The thermal properties of the *syndiotactic*-H-poly(DCPD) samples just described are entirely analogous to those with a syndiotacticity as high as 80% described in papers by Hayano.¹⁰ Similar studies have been published on *isotactic*-H-poly(DCPD) (as high as 95% *isotactic*).³ The most significant difference between the properties of *syndiotactic*-H-poly(DCPD) described briefly here and what has been reported in the literature are the high crystallinities (as high as 0.83 here *vs.* 0.61 for 80% syndiotactic poly(DCPD) described in the literature^{3b}), as one might expect from a polymer that is closer to a 100% *syndiotactic* structure.

Conclusions

W(N-*t*-Bu)(CHCMe₃)(pyr)(OHMT) (**2**), W(N-2,6-*i*-Pr₂C₆H₃)(CHCMe₂Ph)(pyr)(OHMT) (**3**), W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(PMePh₂) (**7**), W(O)(CHCMe₂Ph)(Me₂Pyr)(ODFT)(PMePh₂) (**9**), and W(O)(CHCMe₂Ph)(Me₂Pyr)(OTPP)(PMePh₂) (**10**) all produce poly(DCPD)s that have *cis,syndiotactic* structures. *Cis,isotactic*-poly(DCPD)s can be prepared from the biphenolate alkylidene complexes Mo(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(*rac*-biphen) (**17**) and W(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(*rac*-biphen) (**22**). The molybdenum-based complex Mo(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(THF)(*rac*-biphen) (**20**) will also yield *cis,isotactic*-poly(DCPD) in the presence of 5 mol% 1-hexene. Polymers are accessible within minutes at room temperature, no isomerization or cross-linking reactions were observed, and the addition of a chain transfer reagent or the use of coordinating solvents such as THF do not decrease the selectivity of the initiators. Stereospecificities also are not altered upon addition of a chain transfer reagent. Hydrogenation of the highly tactic poly(DCPD)s allows hydrocarbon polymers that have high crystallinities and melting points to be accessed readily. Finally, this work suggests that the principles of forming isotactic poly(DCPD) from biphenolates and binaphtholates or syndiotactic poly(DCPD) from MAP initiators applies to DCPD and therefore is likely to extend to other norbornene related monomers.

Experimental

General

ROMP reactions were conducted under N₂ in a glovebox. *Endo*-dicyclopentadiene was purchased from Sigma-Aldrich and was distilled prior to use. *p*-Toluenesulfonyl hydrazide (*p*-Tos-NHNH₂) was purchased from Sigma-Aldrich and was used without further purification.

Mo(NAr)(CHCMe₂Ph)(O-*t*-Bu)₂ (**1**; NAr = N-2,6-*i*-Pr₂C₆H₃),¹⁸ W(N-*t*-Bu)(CHCMe₃)(pyr)(OHMT) (**2**, OHMT = O-2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃),¹⁹ W(NAr)(CHCMe₂Ph)(pyr)(OHMT) (**3**),²⁰ W(N-2,6-Me₂C₆H₃)(C₃H₆)(pyr)(OHIPT) (**4**, OHIPT = O-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃),²¹ W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(PMePh₂) (**7**),²² W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(MeCN) (**8**),²² W(O)(CHCMe₂Ph)(Me₂Pyr)(ODFT)(PMePh₂) (**9**, DFTO = O-2,6-(C₆F₅)₂C₆H₃),^{22,9b} W(O)(CHCMe₂Ph)(Me₂Pyr)(OTPP)(PMePh₂) (**10**, OTTP = O-2,3,5,6-Ph₄C₆H),^{22,9b} Mo(N-*t*-Bu)(CHCMe₃)(pyr)(OHMT) (**12**),¹⁹ Mo(NAd)(CHCMe₃)(pyr)(OHMT) (**13**; Ad = 1-adamantyl),¹⁹ Mo(NAr)(CHCMe₂Ph)(Me₂pyr)(ODPP) (**14**),²³ Mo(NAr)(CHCMe₂Ph)(pyr)(OHMT) (**15**),²⁴ Mo(N-2,6-Me₂C₆H₃)(CHCMe₃)(pyr)(OHIPT) (**16**),²⁰ Mo(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(*rac*-biphen) (**17**, biphen = 3,3'-(*t*-Bu)₂-5',6,6'-(CH₃)₄-1,1'-biphenyl-2,2'-diolate)²⁵, Mo(NAr)(CHCMe₂Ph)(*rac*-biphen-*t*-Bu) (**18**, biphen-*t*-Bu = 3,3'-(*t*-Bu)₂-5,5'-(*t*-Bu)₂-6,6'-(CH₃)₂-1,1'-biphenyl-2,2'-diolate),²⁵ Mo(NAd)(CHCMe₂Ph)(*rac*-biphen-*t*-Bu) (**19**),²⁵ Mo(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(THF)(*rac*-biphenCF₃) (**20**, biphenCF₃ = 3,3'-(*t*-Bu)₂-5,5'-(CF₃)₂-6,6'-(CH₃)₂-1,1'-biphenyl-2,2'-diolate),²⁵ Mo(NAd)(CHCMe₂Ph)(THF)(*rac*-biphenCF₃) (**21**),²⁵ W(N-2,6-Me₂C₆H₃)(CHCMe₂Ph)(*rac*-biphen) (**22**),²⁶ W(O)(CHCMe₂Ph)(OHMT)₂ (**23**),^{9b} W(O)(CHCMe₂Ph)(OTPP)₂(PMePh₂) (**24**),^{9b} W(NC₆F₅)(CHCMe₃)(ODFT)₂ (**25**),¹¹ W(N-2,4,6-Cl₃C₆H₂)(CHCMe₃)(O-2,6-(CHPh₂)₂-3-MeC₆H₂)₂ (**26a**),²⁷ W(N-2,4,6-Br₃C₆H₂)(CHCMe₃)(O-2,6-(CHPh₂)₂-3-MeC₆H₂)₂ (**26b**),²⁷ W(N-2,4,6-Cl₃C₆H₂)(CHCMe₃)(OTf)₂(dme),²⁷ and W(O)(CHCMe₂Ph)(Me₂Pyr)₂(PPh₂Me)²⁸ were prepared according to published procedures.

NMR spectra were recorded on a 400 MHz (¹H) spectrometer in CDCl₃ at 25°C and 55°C or in C₂D₂Cl₄ at 140°C and data are listed in parts per million (ppm) downfield from

tetramethylsilane (TMS) as an internal standard. For ^1H NMR: CDCl_3 7.26 ppm, $\text{C}_2\text{D}_2\text{Cl}_4$ 5.97 ppm. For ^{13}C NMR: CDCl_3 77.00 ppm, $\text{C}_2\text{D}_2\text{Cl}_4$ 73.88 ppm.

Differential scanning calorimetry (DSC) measurements were performed under N_2 in a TA Instruments Q-2000 calorimeter. The heating rate was 10 K/min and the cooling rate was 20 K/min for each cycle.

Wide angle x-ray diffraction spectra were recorded on a Rigaku D/Max Rapid II diffractometer in transmission mode (Cu, 40 kV; 2Θ : 5 – 100°; ω =0°C; 80 μm dia. collimator). The polymer sample was compressed to a compact pellet prior to measurement (3 bar, 1 min) and data were collected for 1h.

Synthesis of $\text{W}(\text{N-2,4,6-Cl}_3\text{C}_6\text{H}_2)(\text{CHCMe}_3)(2,5\text{-Me}_2\text{pyr})_2$

$\text{W}(\text{N-2,4,6-Cl}_3\text{C}_6\text{H}_2)(\text{CHCMe}_3)(\text{OTf})_2(\text{dme})$ (1.0g, 1.20 mmol) was charged to a flask containing 40 mL of toluene and ~1 mL of DME. The resulting solution was chilled at -30°C for two hours. LiMe_2pyr (254 mg, 2.51 mmol) was then added to the stirred solution and the resulting mixture was allowed to stir for 1.5 h. Solvent was removed under vacuum and the residue was charged with CH_2Cl_2 . The mixture was filtered through Celite and the Celite was washed with CH_2Cl_2 . The solvent was removed from the filtrate *in vacuo* to give an orange solid (641mg, 84%) ^1H NMR (C_6D_6 , 500 MHz) δ 11.02 (bs, 1H, W=CH), 6.81 (s, 2H, Ar), 6.03 (brs, 4H, pyr), 2.26 (bs, 12H, pyr), 1.21 (s, 9H, Me_3); ^{13}C NMR (125 MHz) 288.14 (W=C), 148.89, 132.52, 130.21, 128.48, 128.34, 107.62, 48.42, 33.83, 18.62. Anal. Calcd (%) for $\text{C}_{23}\text{H}_{28}\text{Cl}_3\text{N}_3\text{W}$: C 43.39, H 4.43, N 6.60. Found: C 43.11, H 4.31, N 6.41.

Synthesis of $\text{W}(\text{N-2,4,6-Cl}_3\text{C}_6\text{H}_2)(\text{CHCMe}_3)(\text{Me}_2\text{pyr})(\text{OHMT})$ (5)

$\text{W}(\text{N-2,4,6-Cl}_3\text{C}_6\text{H}_2)(\text{CHCMe}_3)(2,5\text{-Me}_2\text{pyr})_2$ (250 mg, 0.393 mmol) was charged to a flask containing 40 mL of diethyl ether, and the resulting solution was chilled for one hour at -30 °C. HMTOH (130 mg, 0.393 mmol) was added and the solution was allowed to stir and warm to room temperature overnight. The solvents were removed from the solution *in vacuo* and a small amount of pentane was added to the resulting residue and the mixture was filtered to give a

yellow solid (119 mg, 35%). The filtrate was concentrated and put in the freezer to isolate a pure second crop of product: ^1H NMR (C_6D_6 , 500 MHz) 8.40 (s, 1H, W=CH, $^1J_{\text{WC}} = 115$ Hz (*syn*), $^2J_{\text{WH}} = 16.5$ Hz), 6.93 (m, 3H, OHMT), 6.81 (s, 4H, OHMT), 6.80 (s, 2H, Ar), 6.06 (s, 2H, pyr), 2.14 (s, 12H, OHMT), 2.11 (s, 6H, pyr), 2.03 (s, 6H, OHMT), 1.13 (s, 9H, CMe_3); ^{13}C NMR (125 MHz) 269.28 (W=CH), 157.98, 149.47, 137.18, 136.84, 136.51, 135.04, 132.27, 130.41, 129.71, 129.49, 128.65, 127.70, 123.80, 110.29, 46.22, 33.10, 21.33, 21.21, 20.49.

Synthesis of **W(N-2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$)(CHCMe₃)(Me₂pyr)(ODFT) (6)**

W(N-2,4,6- $\text{Cl}_3\text{C}_6\text{H}_2$)(CHCMe₃)(2,5-Me₂pyr)₂ (304 mg, 0.477 mmol) was added to a flask containing 20 mL of diethyl ether and the solution was chilled to -30 °C for 45 min. DFTOH (203 mg, 0.477 mmol) was added to the stirred mixture in 2 mL of diethyl ether dropwise. After 1 h, the volatiles were removed and small amount of pentane was added to the resulting residue and the mixture was filtered to give 239 mg; further crystallization from the filtrate gave another 101mg; total 340mg (74%): ^1H NMR (C_6D_6 , 500 MHz) 8.87 (s, 1H, W=CH, $^1J_{\text{WC}} = 110\text{Hz}$, $^2J_{\text{WH}} = 15.5$ Hz), 7.09 (d, 2H, ODFT), 6.85 (t, 1H, ODFT), 6.61 (s, 2H, Ar), 5.87 (bs, 2H, Me₂pyr), 2.11 (bs, 6H, Me₂pyr), 0.93 (s, 9H, CMe_3); ^{13}C NMR (125 MHz): 270.46 (W=CH, $^1J_{\text{WC}} = 190\text{Hz}$), 163.07, 148.86, 145.67 (m), 143.71 (m), 142.26 (m), 140.44 (m), 139.25 (m), 137.26 (m), 133.73, 132.15, 131.21, 127.95, 123.09, 118.02, 111.67 (td), 110.98, 65.95, 46.77, 32.44; ^{19}F NMR (282 MHz): -140.01 (d, 2F, *ortho*), -140.54 (d, 2F, *ortho*), -153.09 (t, 1F, *para*), -161.38 (m, 2F, *meta*). Anal. Calcd (%) for $\text{C}_{35}\text{H}_{23}\text{Cl}_3\text{F}_{10}\text{N}_2\text{OW}$: C 43.44, H 2.40, N 2.89. Found C 43.50, H 2.33, N 2.73.

In situ generation of **W(O)(CHCMe₂Ph)(Me₂Pyr)(ODPP) (11, ODPP = O-2,6-Ph₂C₆H₃)**

A solution of DPPOH (3.6 mg, 13.4 μmol ; in 0.3 mL C_6D_6) was added to a solution of W(O)(CHCMe₂Ph)(Me₂Pyr)₂(PPh₂Me) (10.0 mg, 14.6 μmol) in C_6D_6 (0.7 mL). The bright orange mixture was heated to 65°C for 4 h during which time a color change to yellow was observed. Full conversion was confirmed via ^1H NMR spectroscopy with the appearance of an alkylidene resonance at 10.36 ppm (s) for W(O)(CHCMe₂Ph)(Me₂Pyr)(ODPP) (instead of the

resonance at 9.83 ppm for $W(O)(CHCMe_2Ph)(Me_2Pyr)_2(PPh_2Me)$.

Polymer syntheses

All polymerizations were performed at room temperature. A solution of an initiator in dichloromethane was added in one portion (0.5 – 2.0 mol% catalyst in 0.2 mL CH_2Cl_2) to a stirred dichloromethane solution containing 2 wt% DCPD (20 mg DCPD/1g CH_2Cl_2). Benzaldehyde was added after a specific period of time (Table 1) and the poly(DCPD)s were precipitated from methanol and all solvents were removed *in vacuo*.

Cis, syndiotactic poly(DCPD)

1H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 5.69 (s, 1H) 5.55 (s, 1H), 5.38-5.28 (m, 2H), 3.32 (s, 1H), 2.90-2.85 (m, 3H), 2.37-2.21 (m, 2H), 1.70-1.62 (m, 1H), 1.29-1.20 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$, 25°C) δ 132.42, 132.15, 131.53, 131.17, 130.84, 55.09, 54.94, 45.01, 44.86, 42.19, 41.54, 39.08, 34.72 ppm.

Cis, isotactic poly(DCPD)

1H NMR (400.13 MHz, $CDCl_3$, 25°C) δ 5.67 (s, 1H) 5.53 (s, 1H), 5.35-5.26 (m, 2H), 3.23 (s, 1H), 2.86 (broad s, 3H), 2.34-2.27 (m, 2H), 1.59 (s, 1H), 1.24-1.19 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $CDCl_3$, 25°C) δ 132.65, 132.48, 131.64, 131.49, 130.75, 55.63, 45.39, 45.28, 42.40, 42.23, 41.56, 38.78, 34.79 ppm; ^{13}C NMR (100.61 MHz, $C_2D_2Cl_4$, 140°C) δ 132.49, 132.31, 131.57, 131.37, 131.15, 130.73, 55.67, 55.58, 45.56, 45.47, 42.43, 42.33, 41.71, 39.19, 34.72 ppm.

Hydrogenation of poly(DCPD)

Hydrogenation reactions were performed at 130 °C in a pressure tube. Four equivalents of *p*-Tos-NHNH₂ per DCPD were added to a chloroform solution containing 2 wt% poly(DCPD). The reaction was stirred vigorously for 6 h. The reaction mixture was allowed to cool to room temperature and was poured into excess methanol. The polymer was rinsed repeatedly with methanol and all solvents were removed from the H-poly(DCPD) samples *in vacuo*.

Syndiotactic H-poly(DCDP)

^1H NMR (400.13 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 140°C) δ 2.50 (s, 2H), 1.84 (s, 2H), 1.64 (s, 4H), 1.47 - 1.32 (m, 7H), 0.96 - 0.80 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 140°C) δ 46.27, 42.95, 37.28, 30.27, 28.11, 27.46 ppm.

Isotactic H-poly(DCDP)

^1H NMR (400.13 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 140 °C) δ 2.50 (s, 2H), 1.86 (s, 2H), 1.65 (s, 4H), 1.42 - 1.32 (m, 7H), 1.00 - 0.81 (m, 1H) ppm; ^{13}C NMR (100.61 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 140 °C) δ 46.24, 42.89, 37.22, 30.26, 28.07, 27.43 ppm.

Acknowledgments R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) for research support and Dr. Jeffrey H. Simpson and Anne M. Rachupka for their help with NMR experiments.

Supporting Information Available Complete proton NMR spectra, carbon NMR spectra, COSY spectra, DSC, and WAX data for all polymers prepared here (Tables S1-S7 and Figures S1-S40).

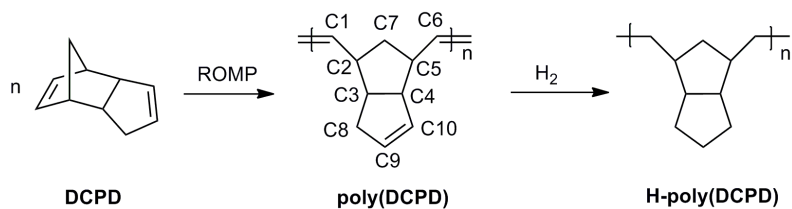


Figure 1. Formation of poly(DCPD) and its hydrogenated version, H-poly(DCPD).

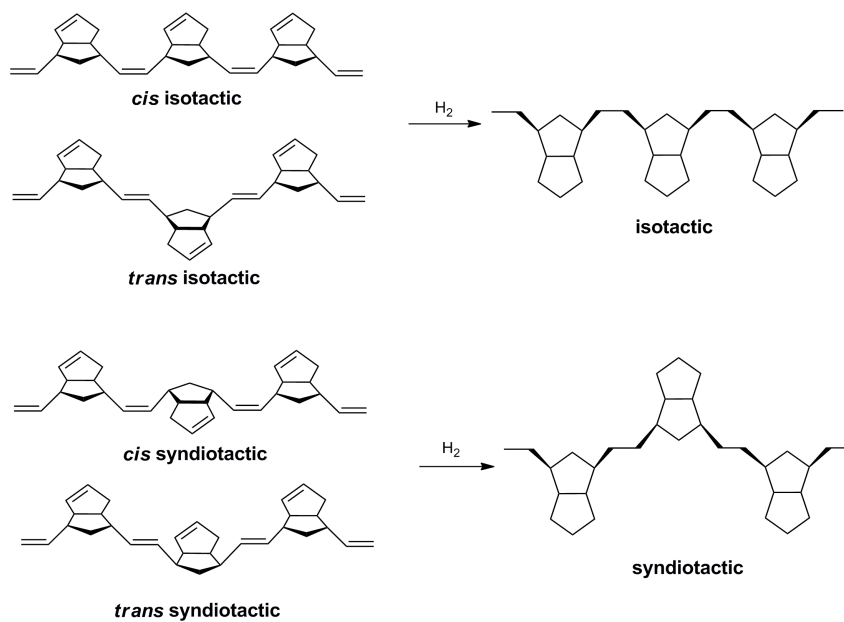


Figure 2. Possible structures of poly(DCPD) and hydrogenated polymers.
(The cyclopentene C=C bond is drawn at random in these structures.)

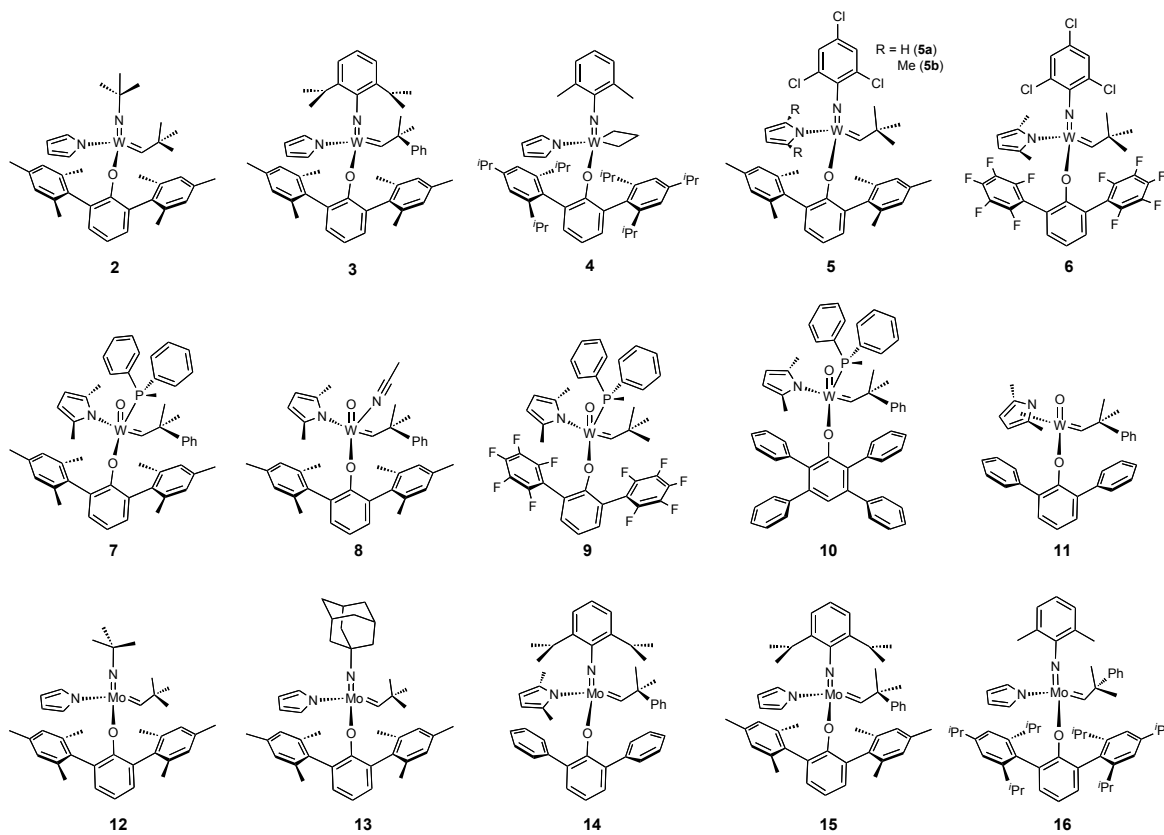


Figure 3. MAP alkylidene initiators **2** – **16** employed for formation of *cis,syndiotactic*-poly(DCPD).

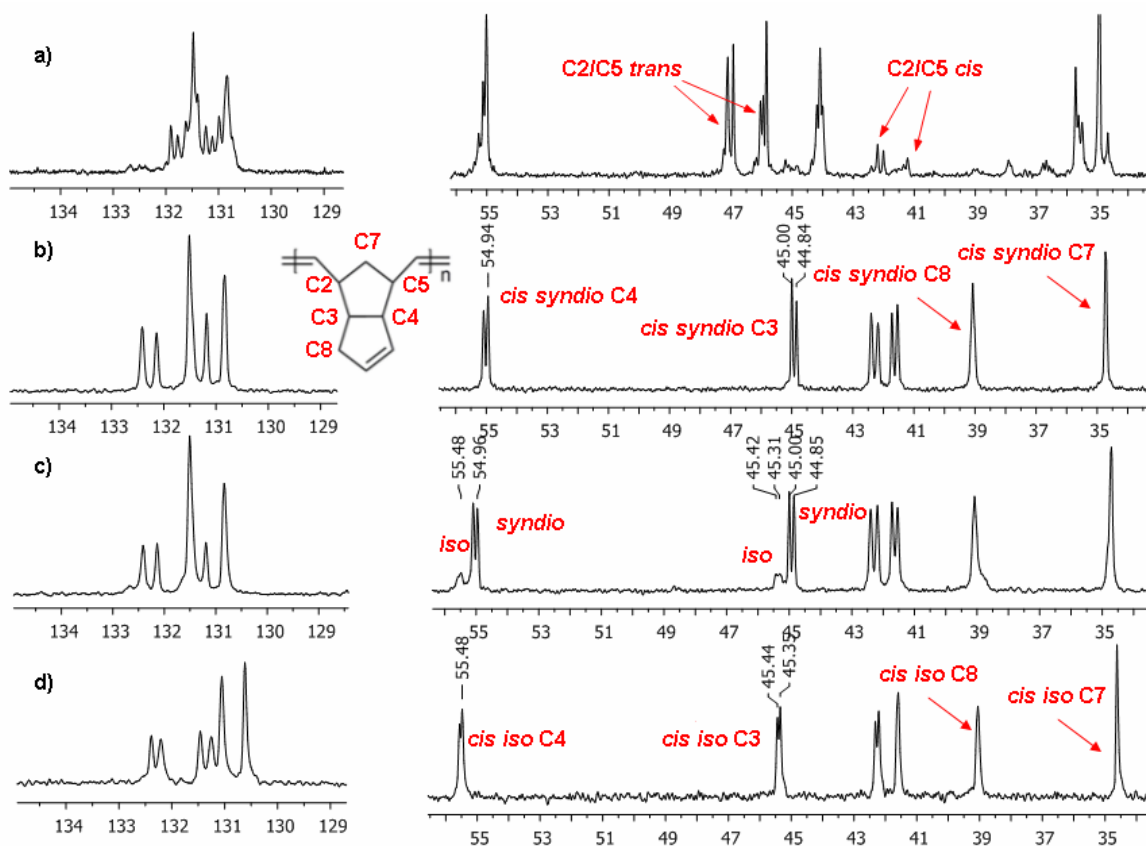


Figure 4. ^{13}C NMR spectra (100.61 MHz) of (a) atactic poly(DCPD) derived from **1**; (b) *cis,syndiotactic*-poly(DCPD) derived from **2**; (c) 100% *cis*, 70% *syndiotactic*-poly(DCPD) derived from **8**; (d) *cis,isotactic*-poly(DCPD) derived from **20(hex)** (**20** in the presence of 1-hexene as a chain transfer agent). Full spectra can be found in the SI.

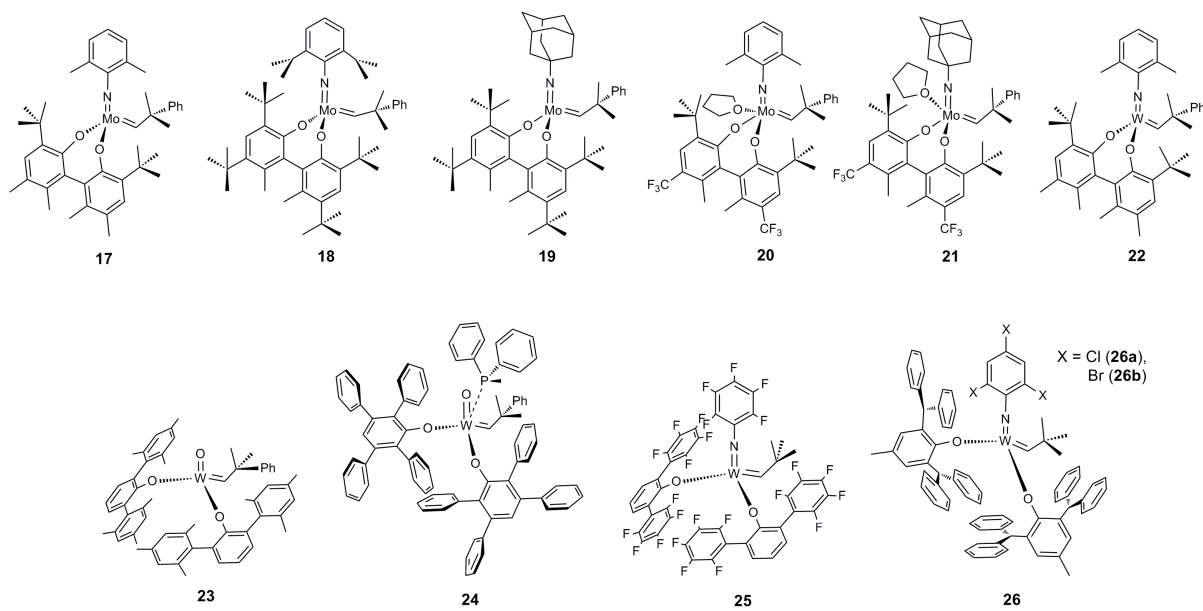


Figure 5. Biphenolate and bisaryloxide alkylidene initiators **17 – 26** employed for formation of *cis, isotactic*-poly(DCPD).

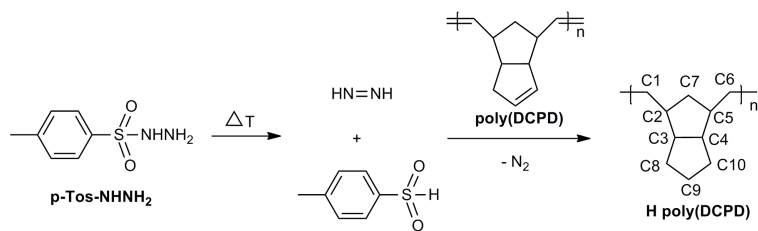


Figure 6. Hydrogenation of poly(DCPD) with diimine generated *in situ*.

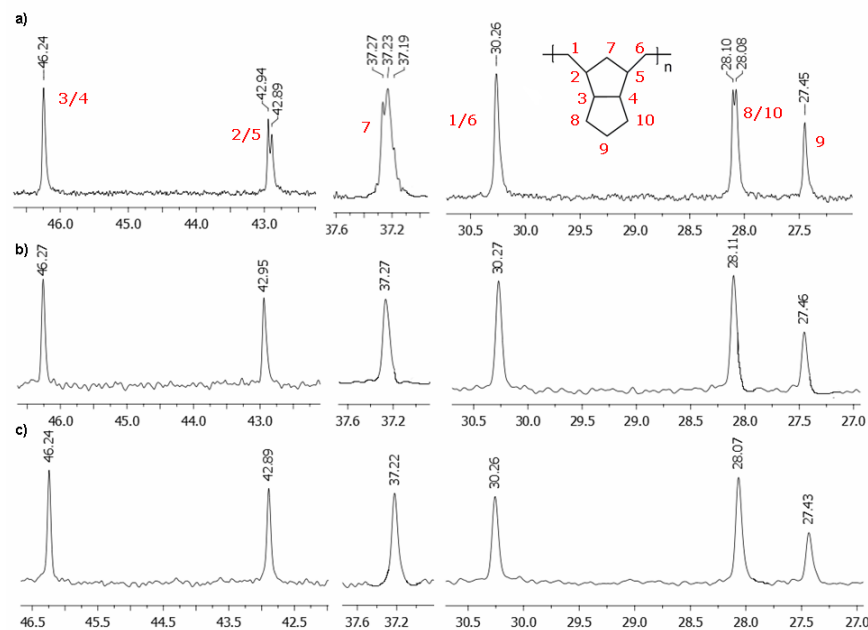


Figure 7. ^{13}C NMR spectra of (a) atactic H-poly(DCPD) derived from poly(DCPD) made from **12**; (b) syndiotactic-H-poly(DCPD) derived from poly(DCPD) made from **2**; (c) isotactic-H-poly(DCPD) derived from poly(DCPD) made from **20(hex)**. Full spectra can be found in the SI.

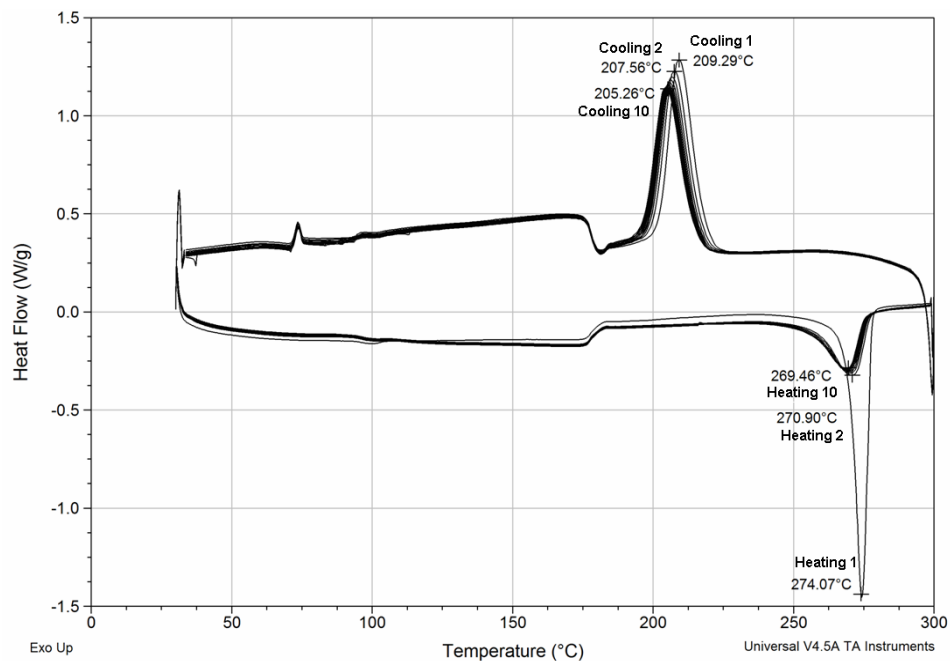


Figure 8. DSC thermogram (ten heating/cooling cycles) of syndiotactic-H-poly(DCPD) (50 equiv DCPD, Table 4) prepared from **2**. Heating rate = 10 $^{\circ}\text{C}/\text{min}$; cooling rate = 20 $^{\circ}\text{C}/\text{min}$.

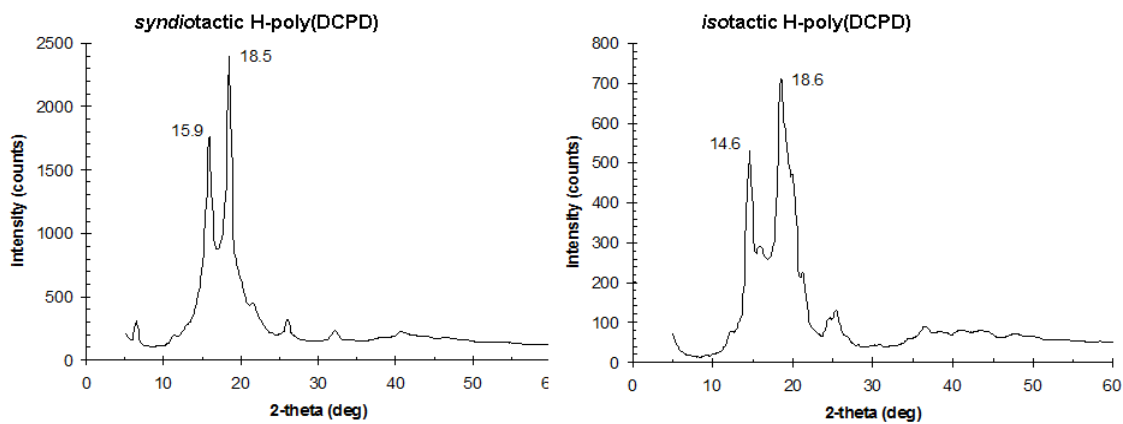


Figure 9. WAX diffraction patterns of *syndiotactic*-H-poly(DCPD) prepared from **2** ($w_c = 0.83$) and *isotactic*-H-poly(DCPD) prepared from **20(hex)** ($w_c = 0.74$).

Table 1. Polymerization of DCPD with catalysts **1 – 26**.

Catalyst	Equiv. DCPD ^a	Time ^b	cis [%] ^c	Tacticity ^c
1	100	1 min	18	55% <i>iso</i>
	200	2 min	20	57% <i>iso</i>
2	50	30 sec	100	100% <i>syndio</i>
	100	1 min	100	100% <i>syndio</i>
	200	<3 min	100	100% <i>syndio</i>
3	50	1 min	100	100% <i>syndio</i>
	100	<3 min	100	100% <i>syndio</i>
	200	5 min	100	100% <i>syndio</i>
4	50	25 min	85	70% <i>syndio</i>
	100	60 min	83	73% <i>syndio</i>
5	50	1 min	90	90% <i>syndio</i>
6	50	30 sec	100	66% <i>syndio</i>
7	50	1 min	100	100% <i>syndio</i>
	100	<2 min	100	100% <i>syndio</i>
8	50	1 min	100	75% <i>syndio</i>
	100	<2 min	100	78% <i>syndio</i>
9	50	<30 sec	100	100% <i>syndio</i>
	100	30 sec	100	100% <i>syndio</i>
	200	< 2 min	100	100% <i>syndio</i>
10	50	1 min	100	100% <i>syndio</i>
	100	<2 min	100	100% <i>syndio</i>
	200	<3 min	100	100% <i>syndio</i>
11	50	2 min	100	90% <i>syndio</i>
12	100	30 sec	68	55% <i>syndio</i>
13	100	30 s	62	53% <i>syndio</i>
14	200	30 s	--- ^d	---
15	100	< 2 min	80	90% <i>syndio</i>
	200	< 5 min	83	90% <i>syndio</i>
16	100	5 min	60	---
17	100	30 sec	100	100% <i>iso</i>
18	100	30 sec	100	90% <i>iso</i>
19	100	30 sec	100	75% <i>iso</i>
20	50	<20 sec	90	>95% <i>iso</i>
	100	30 sec	90	>95% <i>iso</i>

	200	<1 min	87	91% <i>iso</i>
21	100	30 sec	85	70% <i>iso</i>
22	100	30 sec	100	100% <i>iso</i>
23	50	30 min	100	70% <i>syndio</i>
24	50	3 min	100	70% <i>iso</i>
25	50	<30 sec	100	70% <i>iso</i>
	100	<1 min	100	73% <i>iso</i>
26a	50	3 min	100	70% <i>iso</i>
26b	50	2 min	81	63% <i>iso</i>

^a With respect to each equivalent of catalyst. ^b Time required for >99% monomer conversion.

^c Determined by ¹³C NMR. ^d Not determined due to partial insolubility or unclear NMR spectra.

Table 2. ROMP of DCPD in the presence of 1-hexene.

Initiator ^a	Equiv DCPD	Equiv 1-hexene	Tacticity
2	1000	50	<i>cis,syndio</i>
7	1000	50	<i>cis,syndio</i>
	5000	250	<i>cis,syndio</i>
9	1000	50	<i>cis,syndio</i>
	10000	500	<i>cis,syndio</i>
17	1000	50	<i>cis,iso</i>
	50000	2500	<i>cis,iso</i>
20	1000	50	<i>cis,iso</i>
	50000	2500	<i>cis,iso</i>
22	10000	500	<i>cis,iso</i>

^a 22 °C, CH₂Cl₂. Tacticity determined *via* ¹³C NMR.

Table 3. k_p/k_i values for selected initiators reacting with DCPD (8 equiv) at 22°C in CD_2Cl_2 .

Initiator	2	7	9	13	12	20	17	22
k_p/k_i	1.1	4.2	7.4	14.3	13.2	23.1	16.4	3.3
Tacticity	<i>c,s</i> ^a	<i>c,s</i>	<i>c,s</i>	<i>atactic</i>	<i>atactic</i>	85% <i>c,i</i> ^b	<i>c,i</i>	<i>c,i</i>

^a*Cis,syndiotactic* ^b*Cis,isotactic***Table 4.** Physical properties of tactic H-poly(DCPD)s.

Catalyst	Equiv. DCPD	Tacticity	Thermal properties [°C] ^a			w_c ^b
			T_g	T_m	T_c	
2	50	<i>syndio</i>	96	274 (56 J/g)	209 (-32 J/g)	0.83
2	100	<i>syndio</i>	97	272 (56 J/g)	201(-25 J/g)	0.80
2	200	<i>syndio</i>	97	278 (55 J/g)	168(-45 J/g)	0.83
9(hex)	1000 (5% 1-hex)	<i>syndio</i>	96	272 (46 J/g)	230 (-45 J/g)	0.82
17	50	<i>iso</i>	97	290 (54 J/g)	180 (-25 J/g)	0.69
17	100	<i>iso</i>	97	293(52 J/g)	173(-24 J/g)	0.55
20(hex)	1000 (5% 1-hex)	<i>iso</i>	97	288 (58 J/g)	^c	0.74

^a First scan of the DSC measurement. ^b Crystallinity fraction (w_c) evaluated by separating the crystalline peaks and the amorphous halo of the WAXRD pattern. ^c Not observable.

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Table of Contents Graphic

for

**Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of
Endo-Dicyclopentadiene by Molybdenum and Tungsten Catalysts**

Benjamin Autenrieth, Hyangsoo Jeong, William P. Forrest, Jonathan C. Axtell, Antje Ota,
Thomas Lehr, Michael R. Buchmeiser, and Richard R. Schrock

