Syndioselective Ring-Opening Metathesis Polymerization of *endo*-Dicyclopentadiene with Tungsten Complexes Having Imido Ligands: Development of Crystalline Syndiotactic Hydrogenated Poly(*endo*-dicyclopentadiene)

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Received September 27, 2005; Revised Manuscript Received October 30, 2005

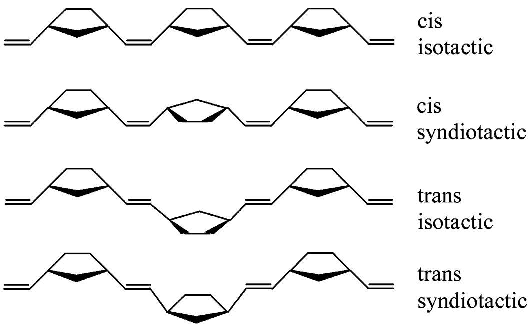
ABSTRACT: Tungsten-based catalysts induced syndioselective ring-opening metathesis polymerization (ROMP) of *endo*-dicyclopentadiene (DCPD) to produce a new class of crystalline polymer. Various tungsten(VI) imido chloride complexes of the type $W({=}N{-}R)Cl_4{\cdot}(Et_2O)_n$ (R = Ph, 2,6-Me_2Ph, α-naphthyl, 2,6-*i*-Pr_2Ph, Et, *n*-Bu, *n*-Hex, cyclohexyl, adamantyl; $n = 0$ or 1) were prepared, which in combination with $Et_2Al(OEt)$ efficiently induced ROMP of DCPD. $W({=}N{-}Ph)Cl_4{\cdot}Et_2O$ and $W({=}N{-}Et)Cl_4{\cdot}Et_2O$ promoted *cis*- and syndioselective ROMP of DCPD, and the following hydrogenation provided a new crystalline polymer, syndiotactic hydrogenated poly(DCPD), which was characteristic in high melting point and in high crystallinity ($T_m = 270$ °C, $\Delta H = 52$ J/g, $w_c = 0.61$). The syndioselectivity of the polymerization could be controlled in the range 30−80% by the suitable choice of those tungsten imido catalysts. These are the first examples of well-designed binary catalysts that are effective in the syndioselective ROMP of DCPD.

Introduction

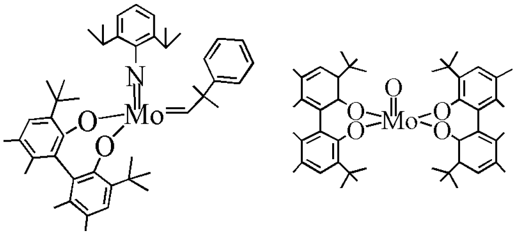
In general, conventional polymeric materials synthesized via the addition polymerization mechanism are assemblies of macromolecules with different molecular weights and steric structures. The properties of such polymers are the average of those of each macromolecule. Thus, it is necessary for the improvement of their performances to precisely control their molecular weight, molecular weight distribution, regioregularity, and stereoregularity. For these reasons, precise polymerization has been researched a great deal for the purpose of developing new, versatile polymeric materials. The precise ring-opening metathesis polymerization (ROMP) of cycloolefins has also been under intensive research.[1,2] It has been recognized that the development of well-defined catalysts enabled the living and/or stereospecific ROMP and several precise olefin metathesis reactions. For instance, famous Schrock catalysts and Schrock−Hoveyda catalysts, molybdenum (and tungsten) alkylidene complexes, have made significant progress with living and/or stereospecific ROMP and with asymmetric ring-closing metathesis.[3,4] An extensive number of superior ruthenium carbenes (Grubbs' catalysts) have made a great influence upon the metathesis chemistry, including the living ROMP.[5,6]

However, there has been little reported about the stereospecific ROMP in the past decades, as the simultaneous regulation of both *cis* ratio and tacticity is assumed to be fairly complicated. For example, there are four possible structures in the polymer backbone of the ROMPed poly(norbornene) (i.e., *cis*-meso, *cis*-racemo, *trans*-meso, and *trans*-racemo) (Scheme 1). The isospecific ROMP of 2,3-bis(trifluoromethyl)norbornadiene, bis(carboalkoxy)norbornadienes, and several 5,6-disubstituted norbornenes has been investigated in detail.[3,6] Schrock−Hoveyda catalysts, which possess diolate ligand, were especially useful for the isospecific ROMP of these cycloolefins.[3,6b−e] Recently, we have reported that the molybdenum- and tungsten-based catalysts bearing substituted diolate ligands such as oxomolybdenum(VI) bis(*racemic*-5,5′,6,6′-tertamethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diolate) (MoO(*rac*-Biphenolate)$_2$) promoted *cis*- and isospecific ROMP of *endo*-dicyclopentadiene (DCPD) and norbornene (Scheme 2).[7] Isotactic polymer generally would form when the enchainment barrier at one site is significantly lower in energy compared to that of the rest sites. The isospecificity is supposed to originate from the enantiomorphic site control caused by the bulky Biphenolate ligand.[3]

Scheme 1. Structures of ROMPed Poly(norbornene)



Scheme 2. Catalysts for Isospecific ROMP of DCPD



On the other hand, the syndiospecific ROMP of aliphatic cycloolefins is supposed to have been partially unachieved. There are few studies on the syndioselective ROMP of norbornenes. Schrock et al. reported that the special Schrock catalyst was effective for the syndioselective ROMP of 2,3-bis(trifluoromethyl)norbornadiene.[6d] Hamilton and co-workers have uncovered that several classic catalysts attained the

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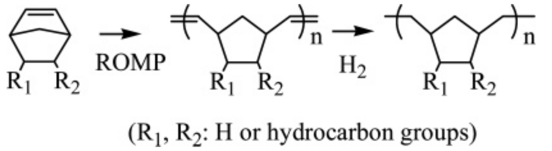
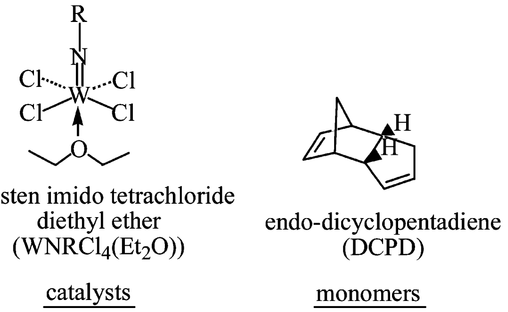
10.1021/ma052088c CCC: \$33.50

Scheme 3. Production of Hydrogenated Poly(cycloolefin)s



Scheme 4. Catalysts and Monomers in This Study



syndioselective ROMP of norbornene.[8] Basset et al. studied the syndioselective ROMP of 1-Me-norbronene by using cyclometalated tungsten aryloxy catalyst.[9] However, the polymerization feature has not been investigated well in these studies, and the correlation between catalyst design and syndioselectivity has not been clarified yet. To summarize the above mentioned, the stereocontrol of ROMP seems to be still worthwhile investigating.

The synthesis and characterization of various hydrogenated poly(cycloolefin)s have been studied in the past.[7,8,10,11] The hydrogenated poly(cycloolefin)s are prepared by ROMP of cycloolefins followed by hydrogenation of double bonds (Scheme 3). Generally, almost all of the hydrogenated poly(cycloolefin)s, except for hydrogenated poly(norbornene), are amorphous when their main chain are atactic. The atactic hydrogenated poly(DCPD) (H-poly(DCPD)) is also an amorphous polymer. On the contrary, isotactic H-poly(DCPD) produced by MoO(*rac*-Biphenolate)$_2$ was a crystalline polymer, which featured high melting point (T_m = 290 °C, ΔH = 42 J/g).[7] However, the syndiotactic H-poly(DCPD) (syndio-H-poly(DCPD)) has not been developed yet, and its properties are still unknown.

These viewpoints led us to the investigation of the syndioselective ROMP of DCPD to uncover the properties of syndiotactic H-poly(DCPD). Our research has focused on (1) the *cis*- and syndioselective ROMP of DCPD by $W(=N-Ph)Cl_4 \cdot Et_2O$ (and $W(=N-Et)Cl_4 \cdot Et_2O$) catalysts, (2) the study of the effect of imido ligand on the stereocontrol of the DCPD polymerization with various $W(=N-R)Cl_4 \cdot Et_2O$, and (3) the characterization of the crystalline syndio-H-poly(DCPD) (Scheme 4). To our best knowledge, this is the first example of the well-designed binary catalysts effective in the syndioselective ROMP of DCPD as aliphatic cycloolefins.[12]

Experimental Section

General Remarks. All operations were carried out in a glovebox (nitrogen atmosphere, O_2 < 1 ppm and H_2O < 1 ppm) or under an argon atmosphere by using standard Schlenk techniques. WCl_6 (Soegawa Chemical), $Et_2Al(OEt)$ (Kanto Chemical), Et_3Al (Kanto Chemical), *i*-Bu_3Al (Kanto Chemical), *n*-Bu_4Sn (Wako Chemical), and *n*-BuLi (Kanto Chemical) were used without further purification. $WOCl_4$ was synthesized from WCl_6 and hexamethyldisiloxane in methylene chloride with reference to the literature.[13] Grubbs catalyst, $Ru(Cy_3P)_2Cl_2(=CHPh)$ (Aldrich), was used as received. Toluene, cyclohexane, *n*-pentane, *n*-hexane, octane, tetrahydrofuran (THF), and diethyl ether were distilled over sodium metal under an argon atmosphere before use. Methylene chloride was distilled over calcium hydride. Hexamethyldisiloxane was distilled over molecular sieves under reduced pressure. Commercially available substituted isocyanates (Tokyo Kasei and Aldrich) were dried over molecular sieves and distilled or only filtrated prior to use. *endo*-Dicyclopentadiene (DCPD) (Zeon Corp.) was distilled over calcium hydride under reduced pressure and stored as cyclohexane solution. 1-Octene (Wako Chemicals) was distilled over calcium hydride.

$W(=N-Ph)Cl_4 \cdot Et_2O$ (1). Freshly purified phenyl isocyanate (1.71 g, 14.4 mmol) was added to a suspension of $WOCl_4$ (4.91 g, 14.4 mmol) in toluene (40 mL). The mixture was heated to reflux while it was stirred for 18 h to give a dark-green suspension. Dark-green microcrystals of crude $(W(=N-Ph)Cl_4)_n$ were collected by centrifugation from this suspension and then washed twice with a small amount of pentane. This material was dissolved in diethyl ether, and the green solution was filtrated and dried in vacuo to yield the desired product of green microcrystals with 90% yield. Recrystallization from diethyl ether/*n*-hexane gave deep-green prism crystals of $W(=N-Ph)Cl_4 \cdot Et_2O$ (**1**). Two crops of corresponding crystals were collected by filtration and dried in vacuo (yield 77% (5.46 g, 11.1 mmol)). ^1H NMR (C_6D_6) δ: 6.97−6.87 (m, 4H, H_{aryl}), 6.16 (t, 1H, H_{aryl}), 4.43 (q, 4H, Et_2O), 1.08 (t, 6H, Et_2O). ^{13}C NMR (C_6D_6) δ: 149.8, 134.0, 131.4, 127.2, 66.3, 13.1. Anal. Calcd for $C_{10}H_{15}Cl_4NOW$: C, 24.47; H, 3.08; N, 2.85. Found: C, 24.24; H, 3.00; N, 2.90.

$W(=N-2,6-Me_2-Ph)Cl_4 \cdot Et_2O$ (2). This complex was prepared and isolated in essentially the same manner as described in the catalyst **1** synthesis section. The desired product was green-brown microcrystals with 91% yield. Recrystallization from diethyl ether/*n*-hexane gave deep-green prism crystals of $W(=N-2,6-Me_2-Ph)Cl_4 \cdot Et_2O$ (**2**). Three crops of the corresponding crystals were collected by filtration and dried in vacuo (yield 79%). ^1H NMR (C_6D_6) δ: 6.73 (d, 2H, H_{aryl}), 5.88 (t, 1H, H_{aryl}), 4.07 (brs, 4H, Et_2O), 3.30 (s, 6H, CH_3), 1.08 (t, 6H, Et_2O). ^{13}C NMR (C_6D_6) δ: 148.3, 145.5, 133.8, 126.1, 65.9, 17.7, 13.8. Anal. Calcd for for $C_{12}H_{19}Cl_4NOW$: C, 27.77; H, 3.69; N, 2.70. Found: C, 27.94; H, 3.76; N, 2.80.

$W(=N-\alpha\text{-naphthyl})Cl_4 \cdot Et_2O$ (3). This complex was prepared and isolated in the manner similar to that in the catalyst **1** synthesis section. The expected product was black microcrystals with 88% yield. Recrystallization from diethyl ether/*n*-hexane gave black needle crystals of $W(=N-\alpha\text{-naphthyl})Cl_4 \cdot Et_2O$ (**3**). The corresponding crystals were collected in two crops by filtration and dried in vacuo (yield 62%). ^1H NMR (C_6D_6) δ: 9.37 (d, 1H, H_{aryl}), 7.15−7.03 (m, 5H, H_{aryl}), 6.36 (d, 1H, H_{aryl}), 4.43 (q, 4H, Et_2O), 1.10 (t, 6H, Et_2O). ^{13}C NMR (C_6D_6) δ: 146.2, 136.5, 135.6, 134.1, 131.0, 130.4, 129.8, 126.9, 122.6, 122.0, 66.5, 13.2. Anal. Calcd for $C_{14}H_{17}C_{l4}NOW$: C, 31.08; H, 3.17; N, 2.59. Found: C, 31.06; H, 3.18; N, 2.68.

$W(=N-2,6\text{-}i\text{-}Pr_2-Ph)Cl_4 \cdot Et_2O$ (4). This complex was prepared and isolated in essentially the same manner as described in the catalyst **1** synthesis section. The crude $(W(=N-2,6\text{-}i\text{-}Pr_2-Ph)Cl_4)_n$ was dissolved in diethyl ether, and the green solution was filtrated and dried in vacuo to yield the desired product of a green-brown powder with 91% yield. Recrystallization from diethyl ether/*n*-hexane gave deep-green needle crystals of $W(=N-2,6\text{-}i\text{-}Pr_2-Ph)Cl_4 \cdot Et_2O$ (**4**). The corresponding crystals were collected by filtration and dried in vacuo (yield 75%). ^1H NMR (C_6D_6) δ: 7.17 (d, 2H, H_{aryl}), 6.24 (t, 1H, H_{aryl}), 4.94 (m, 2H, $CH(CH_3)_2$), 4.35 (q, 4H, Et_2O), 1.34 (d, 12H, CH_3), 1.06 (t, 4H, Et_2O). ^{13}C NMR (C_6D_6) δ: 155.9, 146.3, 134.3, 122.1, 66.0, 27.9, 26.4, 13.1. Anal. Calcd for $C_{16}H_{27}Cl_4NOW$: C, 33.42; H, 4.73; N, 2.44. Found: C, 34.35; H, 4.82; N, 2.53.

$W(=N-Et)Cl_4 \cdot Et_2O$ (5). Freshly purified ethyl isocyanate (0.47 g, 6.6 mmol) was added to a suspension of $WOCl_4$ (2.24 g, 6.6 mmol) in *n*-octane (30 mL). The mixture was heated to reflux while it was stirred for 12 h to give a reddish-orange suspension. Orange microcrystals were collected by centrifugation and washed twice with a small amount of cold pentane to give $(W(=N-Et)Cl_4)_n$ in 86% yield. This material was dissolved in diethyl ether, and the orange solution was filtrated and dried in vacuo to yield the desired product of orange microcrystals with a yield of 84%. Recrystallization was performed from diethyl ether/*n*-hexane to give orange prism crystals of W(═N−Et)Cl_4·Et_2O (**5**). The corresponding crystals were collected in two crops by filtration and dried in vacuo (yield 75%). ^1H NMR (C_6D_6) δ: 6.01 (q, 2H, CH_2), 4.33 (q, 4H, Et_2O), 1.06 (t, 6H, Et_2O), 0.94 (t, 3H, CH_3). ^{13}C NMR (C_6D_6) δ: 65.5, 61.6, 14.6, 13.2. Anal. Calcd for $C_4H_{15}Cl_4NOW$: C, 16.27; H, 3.41; N, 3.16. Found: C, 16.23; H, 3.42; N, 3.12.

W(═N−*n*-Bu)Cl_4·Et_2O (6). This complex was prepared and isolated in the same manner as described in the catalyst W(═N−Et)Cl_4·Et_2O (**5**) synthesis section. The crude (W(═N−*n*-Bu)Cl_4)$_n$ was dissolved in diethyl ether, and the orange solution was filtrated and dried in vacuo to yield the desired product of orange microcrystals with 85% yield. Recrystallization from diethyl ether/*n*-hexane gave orange prism crystals of W(═N−*n*-Bu)Cl_4·Et_2O (**6**). The corresponding crystals were collected in two crops by filtration and dried in vacuo (yield 50%). ^1H NMR (C_6D_6) δ: 6.22 (t, 2H, CH_2), 4.24 (brs, 4H, Et_2O), 1.45 (m, 2H, CH_2), 1.25 (m, 2H, CH_2), 1.06 (t, 6H, Et_2O), 0.65 (t, 3H, CH_3). ^{13}C NMR (C_6D_6) δ: 66.5, 65.5, 32.3, 20.9, 13.5, 13.4. Anal. Calcd for $C_8H_{19}Cl_4NOW$: C, 20.40; H, 4.07; N, 2.97. Found: C, 20.70; H, 4.02; N, 2.97.

W(═N−*n*-Hex)Cl_4 (7). This complex was prepared and isolated in the similar manner as described in the catalyst **5** synthesis section. The expected product was an orange powder with 88% yield. Recrystallization from *n*-hexane gave a fine orange powder of W(═N−*n*-Hex)Cl_4 (**7**). The corresponding powders were collected in four crops by filtration and dried in vacuo (yield 50%). ^1H NMR (C_6D_6) δ: 5.88 (t, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.12 (m, 4H, CH_2), 0.96 (m, 2H, CH_2), 0.81 (t, 2H, CH_3). ^{13}C NMR (C_6D_6) δ: 68.8, 31.2, 30.7, 27.1, 22.7, 14.2. Anal. Calcd for $C_6H_{13}Cl_4NW$: C, 16.96; H, 3.08; N, 3.30. Found: C, 16.99; H, 3.08; N, 3.74.

W(═N−cyclohexyl)Cl_4·Et_2O (8). This complex was prepared and isolated in the same manner as described in the catalyst W(═N-Et)Cl_4·Et_2O synthesis section. The crude (W(═N−cyclohexyl)-Cl_4)$_n$ was dissolved in diethyl ether, and the orange solution was filtrated and dried in vacuo to yield the desired product of orange prism crystals with 90% yield. Recrystallization from diethyl ether/*n*-hexane gave orange prism crystals of W(═N−cyclohexyl)Cl_4·Et_2O (**8**). The corresponding crystals were collected in two crops by filtration and dried in vacuo (yield 86%). ^1H NMR (C_6D_6) δ6.45 (q, 1H, CH), 4.33 (q, 4H, Et_2O), 0.1.83 (m, 4H, CH_2), 1.61 (m, 2H, CH_2), 1.08 (t, 6H, Et_2O), 1.04−0.92 (m, 4H, CH_2); ^{13}C NMR (C_6D_6) 74.9, 65.5, 32.9, 25.2, 23.9, 13.3. Anal. Calcd for $C_{10}H_{21}Cl_4NOW$: C, 24.17; H, 4.26; N, 2.82; Found: C, 24.07; H, 4.25; N, 3.04.

W(═N−adamantyl)Cl_4 (9). Recrystallized 1-adamantyl isocyanate (0.77 g, 4.3 mmol) was added to a suspension of $WOCl_4$ (1.48 g, 4.3 mmol) in *n*-octane (50 mL). The mixture was heated to reflux while it was stirred for 72 h to give a dark-brown suspension. A brownish-yellow powder was collected by filtration, washed five times with a large amount of *n*-hexane, and dried in vacuo to yield the desired product ((W(═N−adamantyl)Cl_4)$_n$ (**9**)) of a brownish-yellow powder (yield 76% (1.55 g, 3.3 mmol)). Recrystallization was not conducted because this material was less soluble in ordinary solvents. ^1H NMR (C_6D_6) δ: 2.0 (brs, 6H, CH_2), 1.93 (brs, 3H, CH_2), 1.19 (brs, 6H, CH_2). ^{13}C NMR (C_6D_6) δ: 77.4, 42.3, 35.2, 29.2. Anal. Calcd for $C_{10}H_{15}Cl_4NOW$: C, 25.29; H, 3.18; N, 2.95. Found: C, 25.00; H, 3.05; N, 3.60.

Analyses of Complex and Polymer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400WB spectrometer (399.65 MHz for ^1H, 100.40 MHz for ^{13}C), and chemical shifts were determined with reference to the residual benzene (δ 7.16 ppm for ^1H, 128.0 ppm for ^{13}C), tetramethylsilane (δ 0.00 ppm), *o*-dichlorobenzene (δ 127.5 ppm), or chloroform (δ 77.2 ppm). Elemental analyses were performed on a PE 2400 series II CHNS/O analyzer. The samples were sealed in tin foils under an argon atmosphere in a glovebox. The molecular weight distributions (MWD) of the polymers were estimated on a gel-permeation chromatograph (GPC) (Tosoh HLC-8121 GPC/HT; eluent *o*-dichlorobenzene). The relative number- and weight-average molecular weights (M_n and M_w, respectively) were calculated by the use of a calibration curve obtained using polystyrene standards. Differential scanning calorimeter (DSC) measurements were performed on a Bruker AXS DSC3100SR in a dry nitrogen stream. Crystallinity of the polymers was estimated on a X-ray diffractometer (XRD) (RIGAKU RINT 2500).

Polymerization. Polymerization was carried out in a prebaked ampule tube equipped with a rubber septum at 50 °C. Polymerization catalyst solutions were prepared as follows unless otherwise stated: A toluene solution of W(═N−Ph)Cl_4·Et_2O (**1**) (0.0278 g, 56.7 μmol) (green solution) was mixed with 3 equiv of $Et_2Al(OEt)$ at room temperature, and the mixture was allowed to be stirred. The mixture was aged for an additional 15 min, resulting in becoming a brown solution. A cyclohexane solution of DCPD (7.50 g, 56.7 mmol) and 1-octene (0.245 g, 2.18 mmol) was added to the mixture at the 50 °C. After stirring for a fixed time, the polymerization was quenched with a small amount of 2-propanol. The polymer yield was determined by gravimetric measurements.

Hydrogenation. A cyclohexane solution of poly(DCPD) and a cyclohexane solution of Ru-based hydrogenation catalyst were mixed in an autoclave under a dry nitrogen atmosphere. Then the dry nitrogen in the autoclave was replaced by dry hydrogen. The mixture was allowed to heat up to the hydrogenation temperature while stirring. Hydrogenation was carried out at 160 °C for 8 h under 1.0 MPa of H_2. After the hydrogenation reaction, the reaction mixture was cooled slowly to room temperature. In the course of this procedure, the recrystallization of syndio-H-poly(DCPD) probably have proceeded from the solution to form the highly crystalline syndio-H-poly(DCPD) as a fine powder. Ru-based hydrogenation catalyst solutions were prepared as follows: Ru-$(Cy_3P)_2Cl_2$(═CHOEt), the precursor of hydrogenation catalyst, was prepared from Ru$(Cy_3P)_2Cl_2$(═CHPh) and 50-fold excess of ethyl vinyl ether. According to the literature, $RuCl_2(H_2)(PCy_3)_2$ or $(PCy_3)_2$ClRu(CO)(H) might be formed in the presence of H_2 and possibly become an active species of hydrogenation.[14]

X-ray Structure Determination of 1 and 8. Single crystals of **1** and **8** suitable for X-ray diffraction were scooped on the loop using sticky liquid paraffin and mounted on a Rigaku RAXIS RAPID imaging plate for data collection using Mo Kα radiation. Crystal data and data collection parameters of these complexes are summarized in Table 1. The data collections were performed at −180 °C. Indexing was performed for three oscillations, and the exposure time was 60 s for each. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A numerical absorption collection was applied, which resulted in transmission factors ranging from 0.32 to 0.66. The data were corrected for Lorentz and polarization effects. The structures of **1** and **8** were solved by direct methods (SIR88[15a] for **1**, SIR92[15b] for **8**) and expanded using Fourier techniques (DIRDIF99[15c]). In the final refinement cycle of the full-matrix least-squares refinement on F^2, all hydrogen atoms were included in the model of at geometrically calculated posistions and refined using a riding model. All non-hydrogen atoms were anisotropically refined. All calculations were performed using the CrystalStructure crystallographic software package. CCDC 279941 contains the supplementary crystallographic data for **1**. CCDC 279940 contains the supplementary crystallographic data for **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis of Tungsten−Imido Tetrachloride. In this study, we have decided to focus our notice on the effects of various imido ligands, which have received little attention so far, on the ROMP catalysts for cyclic olefins. Recently, Schrock and Hoveyda et al. unveiled that the structure of imido ligand played an important role in the control of enantiometric selectivity of ARCM.[3] It is presumable that the steric/electron effect of imido ligand might hold the key in controlling the stereochemistry of asymmetric ring-closing metathesis as well as ROMP. Therefore,

Table 1. Crystal Parameters of W(=N−Ph)Cl_4·Et_2O (1) and W(=N−cyclohexyl)Cl_4·Et_2O (8)

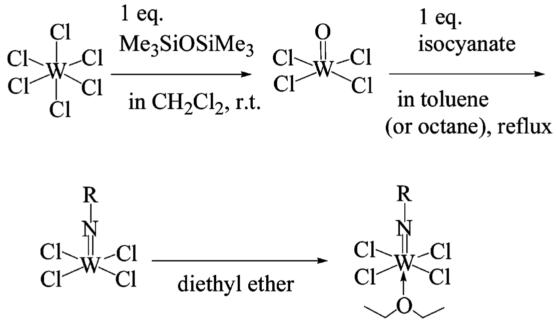
parameter	1	8
chem formula	$C_{10}H_{15}Cl_4NOW$	$C_{10}H_{21}Cl_4NOW$
FW	490.90	496.94
color	green	orange
crystal system	monoclinic	orthorhombic
lattice param.s		
a, Å	19.179(6)	8.1205(14)
b, Å	6.8232(13)	11.170(2)
c, Å	13.841(4)	17.576(3)
α, deg	90	90
β, deg	122.52(2)	90
γ, deg	90	90
V, $Å^3$	1527.3(7)	1594.2(5)
space group	$P2_1/c$	$P2_12_12_1$
Z	4	4
D_{calc}, g/cm^3	2.135	2.070
μ(Mo Kα), cm^{-1}	82.546	79.089
$2\theta_{max}$, deg	60.1	60.1
oscillation range		
($\phi = 0.0°$, $\chi = 45.0°$)	ω 130.0−190.0° with 5.0° step	
($\phi = 90.0°$, $\chi = 45.0°$)		ω 130.0−190.0° with 4.0° step
($\phi = 180.0°$, $\chi = 45.0°$)	ω 0.0−160.0° with 5.0° step	
($\phi = 270.0°$, $\chi = 45.0°$)		ω 0.0−160.0° with 4.0° step
no. of reflections	total: 18058 unique: 4454 (R_{int} = 0.054)	total: 19355 unique: 4668 (R_{int} = 0.054)
no. of observations	4454	4668
no. of variables	169	176
goodness-of-fit on F^2	1.00	1.00
$R1$ (I>2.00σ)	0.020	0.018
R (all reflections)^a	0.037	0.024
$wR2$ (all reflections)^b	0.047	0.035
Flack parameter (Friedel pair = 4269)		−0.009(6)

various tungsten(VI) imido tetrachloride complexes (W(=N−R)Cl_4·$(Et_2O)_n$) were selected as main catalysts. These catalysts were expected to display high ROMP activity because the metal centers of the complexes are in high oxidation states and highly electron deficient. Moreover, steric/electron effects of the imido ligands might influence the stereochemistry of the ROMP distinctly.

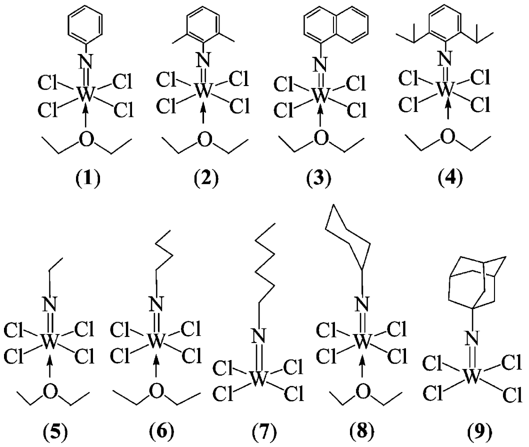
WCl_6 was chosen as a starting material. $WOCl_4$ was synthesized from WCl_6 and hexamethyldisiloxane in methylene chloride.[13] Then $WOCl_4$ as catalyst precursor was treated with an equimolar of isocyanate in toluene (or octane) under reflux condition, and the crude insoluble product of $(W(=N{-}R)Cl_4)_n$ was obtained in a moderate yield (Scheme 5).[16] These products could be recrystallized from suitable solvents such as diethyl ether/*n*-hexane to yield highly pure products of W(=N−R)Cl_4·Et_2O. The following complexes were successfully prepared: W(=N−Ph)Cl_4·Et_2O (**1**), W(=N−2,6-Me_2−Ph)Cl_4·Et_2O (**2**), W(=N−α-naphthyl)Cl_4·Et_2O (**3**), W(=N−2,6-*i*-Pr_2−Ph)Cl_4·Et_2O (**4**), W(=N−Et)Cl_4·Et_2O (**5**), W(=N−*n*-Bu)Cl_4·Et_2O (**6**), W(=N−*n*-Hex)Cl_4 (**7**), W(=N−cyclohexyl)Cl_4·Et_2O (**8**), and W(=N−adamantyl)Cl_4 (**9**) (Scheme 6). ^1H NMR, ^{13}C NMR, and elemental analysis identified these complexes.

Single-crystal X-ray diffraction studies on W(=N−Ph)Cl_4·Et_2O (**1**) and W(=N−cyclohexyl)Cl_4·Et_2O (**8**) were carried out, and their molecular structures are shown in parts a and b of Figure 1, respectively. Selected bond lengths and angles are also stated. The complex **1** has C_1 symmetric distorted octahedral geometry with the phenylimido ligand and diethyl ether in the apical position. The W−N bond length and W−N−C angle indicate the strong donation of the nitrogen lone pair and sp hybridization about the N atom. The C(1)−N(1) distance is 1.378(6) and relatively short, supporting the conjugation system of the phenyl ring with the W−N pseudo triple bond. While, complex **8** is also revealed to have a pseudooctahedral structure, which is similar to that of complex **1**. The relatively short distance of W(1)−N(1) in complex **8** is indicative of a stronger electron donation to metal from the cyclohexyl group and nitrogen. W(1)−O(1) of complex **8** is longer than that of complex **1** as a result of the trans effect from imido ligands. The molecular structures of these two complexes are very similar to the recently reported Mo analogues.[17] Finally, considering the results of X-ray diffraction studies for **1** and **8**, it can be speculated that most of the W(=N−R)Cl_4·Et_2O complexes might have similar C_1 symmetric distorted octahedral structures.

Scheme 5. Synthesis of W−Imido Complexes

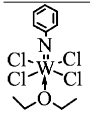
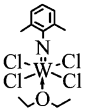
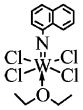
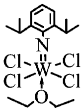


Scheme 6. Tungsten−Imido Chloride Complexes



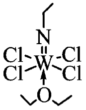
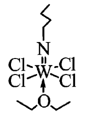
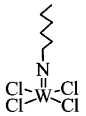
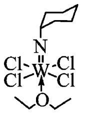
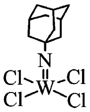
Syndioselective ROMP of DCPD with Several Tungsten−Imido Catalysts and Subsequent Hydrogenation of the Resulting Poly(DCPD). The polymerization activity of W−imido catalysts **1**−**9** was investigated. At first, we performed the **1**-catalyzed polymerization of DCPD without a chain transfer agent. However, the polymerization mixture became very viscous like gel, and the molecular weight of the obtained poly(DCPD) was too high to be determined accurately by GPC. Therefore, we decided to add an adequate amount of 1-octene as a chain transfer reagent in whole the polymerization system, with the purpose of keeping the molecular weight in a moderate range. The **1**−**9** promoted the DCPD polymerizations effectively in the presence of $Et_2Al(OEt)$, giving poly(DCPD)s in quantitative yields. Most of the obtained poly(DCPD)s were highly soluble in ordinary organic solvents, while those produced by **4** and **9** were less soluble at room temperature. Thus, the poly(DCPD)s were characterized by the combination of ^1H NMR

Table 2. Polymerization of DCPD by Various Tungsten−Arylimido Chloride Catalysts and Sequential Hydrogenation of the Obtained Polymers[a]

catalysts		M_n [b], M_w/M_n [b]		poly(DCPD)s		hydrogenated poly(DCPD)s[c]		
							thermal properties	
				cis/trans	T_g,	m/r	1st scan	annealed
	**1**	10 000	3.5	93/7	151 °C	20/80	T_m, 272 °C 52 J/g	T_m, 258 °C 39 J/g
	**2**	27 000	6.0	86/14	149 °C	33/67	T_m, 240 °C 37 J/g	T_m, 234 °C 4 J/g
	**3**	24 000	4.8	89/11	147 °C	36/64	T_g, 101 °C	T_g, 101 °C
	**4**	16 000	3.1	72/28	154 °C	47/53	T_g, 100 °C	T_g, 100 °C

[a] Polymerized in cyclohexane at 50 °C for 3 h; [DCPD] = 1.3 M, [1-octene] = 50 mM, [W complex] = 1.3 mM, [$Et_2Al(OEt)$] = 3.6 mM, all yields are 100%. [b] Before hydrogenation. [c] Hydrogenated in cyclohexane at 160 °C for 8 h; [$Ru(Cy_3P)_2Cl_2({=}CHOEt)$]/[DCPD unit] = 1/1000 in mol ratio, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa.

Table 3. Polymerization of DCPD by Various Tungsten−Alkylimido Chloride Catalysts and Sequential Hydrogenation of the Obtained Polymers[a]

catalysts		M_n [b], M_w/M_n [b]		poly(DCPD)s		hydrogenated poly(DCPD)s[c]		
							thermal properties	
				cis/trans	T_g,	m/r	1st scan	annealed
	**5**	7 600	4.2	90/10	145 °C	20/80	T_m, 270 °C 55 J/g	T_m, 260 °C 42 J/g
	**6**	15 000	3.8	85/15	152 °C	30/70	T_m, 269 °C 41 J/g	T_m, 247 °C 19 J/g
	**7**	9 400	4.2	86/14	140 °C	31/69	T_m, 260 °C 38 J/g	T_m, 248 °C 22 J/g
	**8**	14 000	4.7	78/22	145 °C	37/63	T_g, 101 °C	T_g, 101 °C
	**9**	11 000	3.9	76/24	151 °C	65/35	T_g, 99 °C	T_g, 99 °C

[a] Polymerized in cyclohexane at 50 °C for 3 h; [DCPD] = 1.3 M, [1-octene] = 50 mM, [W complex] = 1.3 mM, [$Et_2Al(OEt)$] = 3.6 mM, all polymer yields are 100%. [b] Before hydrogenation. [c] Hydrogenated in cyclohexane at 160 °C for 8 h; [$Ru(Cy_3P)_2Cl_2({=}CHOEt)$]/[DCPD unit] = 1/1000 in mol ratio, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa.

and GPC at high temperature because all the poly(DCPD)s were entirely soluble at 150 °C. It was found that the M_n of all the poly(DCPD)s was controlled in the range from 7000 to 30 000 g/mol.[18] The ^1H NMR spectra suggested that all the present poly(DCPD)s were linear and non-cross-linked polymers through the selective ROMP of the strained norbornene ring.[19] Further, we have investigated the polymerization of 3,4-dihydro-DCPD by the catalysts **1**−**9**, but no vinyl addition-type oligomer was obtained. This result also supports the complete linearity of the present poly(DCPD)s.

It is noteworthy that the *cis* content of the poly(DCPD) depends on the structure of the tungsten imido catalyst. Table 2 summarizes the results of optimized DCPD polymerization using several W-arylimido catalysts and the subsequent hydrogenation of the obtained poly(DCPD)s. $W({=}N{-}Ph)Cl_4{\cdot}Et_2O$ promoted highly *cis*-regular polymerization (*cis* content > 90%). While the introduction of substituents on the 2,6-position of the phenyl ring obviously gave rise to a decrease in the *cis* ratio of the polymer provided. The poly(DCPD) yielded by **4** was found to be a slightly *cis*-biased polymer, consistent with its low solubility.[20] Table 3 summarized the DCPD polymerization by W alkylimido catalysts. $W({=}N{-}Et)Cl_4{\cdot}Et_2O$, possessing very short *n*-alkyl as an imido substituent, induced *cis*-regular ROMP (cis content > 90%). When W *n*-alkylimido catalysts **6** and **7** were employed, the *cis* contents of the polymerizations were 85% and constant. On the other hand, sterically bulky **8** and **9** promoted the slightly *cis*-biased polymerizations. Similar to the poly(DCPD) from **4**, the poly(DCPD) obtained from **9** was not *cis*-regular and less soluble. To summarize this paragraph, the *cis* content of poly(DCPD)s increased with diminishing the steric size of imido ligands.

With the motivation to know how the structures of the imido affected the stereochemistry of the polymerization (i.e., tacticity of the polymer obtained), hydrogenation of the poly(DCPD)s was then conducted (Tables 2 and 3). Most of the H-poly(DCPD)s were less soluble at room temperature and partially soluble at a high temperature, while the fine powder of H-poly(DCPD)s produced by catalyst **1** and **5** was entirely insoluble in ordinary solvents at room temperature and slightly soluble in *o*-dichlorobenzene at a high temperature. Hence, the tacticities of the H-poly(DCPD)s were determined by ^{13}C NMR at a high temperature (150 °C).

The selected NMR charts of H-poly(DCPD)s under W-arylimido system are illustrated in Figure 2. It is noteworthy that the phenylimido complex **1**, which is sterically uncrowded in the proximity of tungsten, promoted *cis*- and syndioselective ROMP of DCPD. The $W({=}N{-}2,6\text{-}Me_2{-}Ph)Cl_4{\cdot}Et_2O$ (**2**) introduced *cis*- and syndio-biased ROMP. However, the syndioregularity of the polymerization with **2** was lower than that with **1**. Catalyst **3**, whose α-naphthylimido group could be regarded as a 2,3-substituted phenyl group, induced syndio-biased ROMP, and its syndioselectivity was close to that of **2**. Further, the introduction of isopropyl groups on the 2,6-position of the phenyl ring obviously led to the reduction of the syndioselectivity of the polymerization. From these results, it can be said that the syndioregularity decreased with increasing the steric size of substituents on the 2,6-position of the phenyl ring.

In the case of ROMP using the series of aliphatic imido tungsten catalysts, the stereoselectivity was more significantly affected by the structure of the imido ligands (Figure 3). It is also a notable finding that the sterically very small catalyst $W({=}N{-}Et)Cl_4{\cdot}Et_2O$ (**5**) was found to be effective for the *cis*- and syndioselective ROMP. Syndiotactic bias (racemo 70%) was observed in the ^{13}C NMR spectra of the H-poly(DCPD)s prepared by **6** and **7** which possess primary long alkylimido ligands. Interestingly, there was a distinct contrast between the syndioregularity of the polymerization with $W({=}N{-}cyclohexyl)Cl_4{\cdot}Et_2O$ and that with $W({=}N{-}Ph)Cl_4{\cdot}Et_2O$; the cyclohexylimido catalyst **8** exhibited a little ability to regulate the enchainment process (racemo 63%). Beyond our expectation,

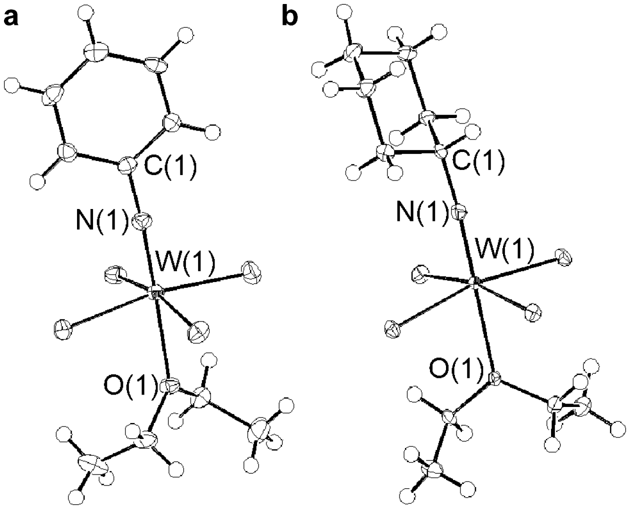


Figure 1. (a) ORTEP representation of W(=N−Ph)Cl_4·Et_2O (**1**) with 50% probability thermal ellipsoids. Selected bond angles and distances: angles (deg), W(1)−N(1)−C(1) = 176.4(2); distances (Å), W(1)−N(1) 1.727(4), N(1)−C(1) = 1.378(6), W(1)−O(1) = 2.280(3). (b) ORTEP representation of W(=N-cyclohexyl)Cl_4·Et_2O (**8**) with 50% probability thermal ellipsoids. Selected bond angles and distances: angles (deg), W(1)−N(1)−C(1) = 173.7(2); distances (Å), W(1)−N(1) 1.696(3), N(1)−C(1) = 1.449(5), W(1)−O(1) = 2.317(2).

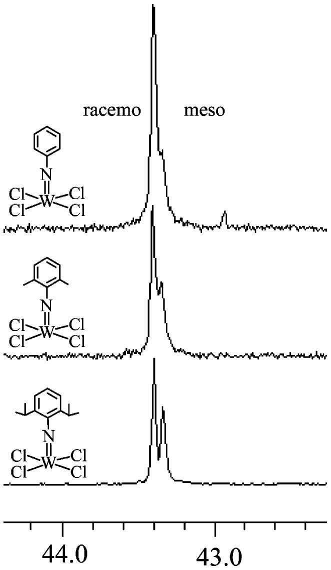


Figure 2. Selected ^{13}C NMR spectra of methyne carbon in the main chain of H-poly(DCPD) with tungsten arylimido catalysts shown in Table 2.

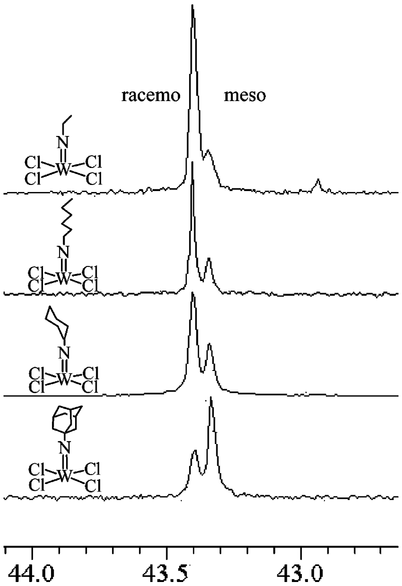


Figure 3. Selected ^{13}C NMR spectra of methyne carbon in the main chain of H-poly(DCPD) with tungsten alkylimido catalysts shown in Table 3.

W(=N−adamantyl)Cl_4 (**9**), whose ligand might fill the vicinity of metal center, produced meso-rich H-poly(DCPD).

It can be concluded that W(=N−Ph)Cl_4·Et_2O (**1**) and W(=N−Et)Cl_4·Et_2O (**5**) induced the syndioselective ROMP of *endo*-dicyclopentadiene. It is very interesting that the present tungsten−imido catalysts seem to be single-site catalysts and to be able to control the polymerization process into syndioselective. Before the present investigation, we suspected that these binary W−imido catalysts would provide the mixture of tactic poly(DCPD) and a certain extent of atactic poly(DCPD), since it is speculated that the $Et_2Al(OEt)$ might alkylate the W−imido complex with violence to produce many kinds of propagating species with different kind/number of ligands. Contrary to our presumption, binary catalysts such as W(=N−Ph)Cl_4·Et_2O−$Et_2Al(OEt)$ successfully promoted the syndioselective polymerization to yield tactic polymer free of any byproducts. This implies that the ligand exchange between W−imido and $Et_2Al(OEt)$ proceeded without any side reaction such as a deprival of imido ligand (vide infra). It is plausible that the strong donation of nitrogen lone pair and the steric hindrance of the imido's substituent decelerated the alkylation reaction and, in turn, depressed the undesirable side reaction.

On the other hand, it has already been reported that W(=O)Cl_4·Et_2O−$Et_2Al(OEt)$ polymerized DCPD smoothly to result in the formation of atactic polymer. In other words, the W(=O)Cl_4·Et_2O is insufficient to regulate the polymerization process. This fact contrasts with the result that the present W−imido catalysts such as W(=N−Et)Cl_4·Et_2O and W(=N−Ph)Cl_4·Et_2O promoted syndioselective ROMP. Taking account of the stated above, it is likely that the imido ligands might play an important role in the regulation of monomer enchainment. However, it remained unknown how the present catalysts control the polymerization process. At least it is assumable that the steric structure of imido ligands might hold the key, and the appropriate matching of the steric structure of imido ligands and the monomer structures would be essential for the precise control of the polymerization.

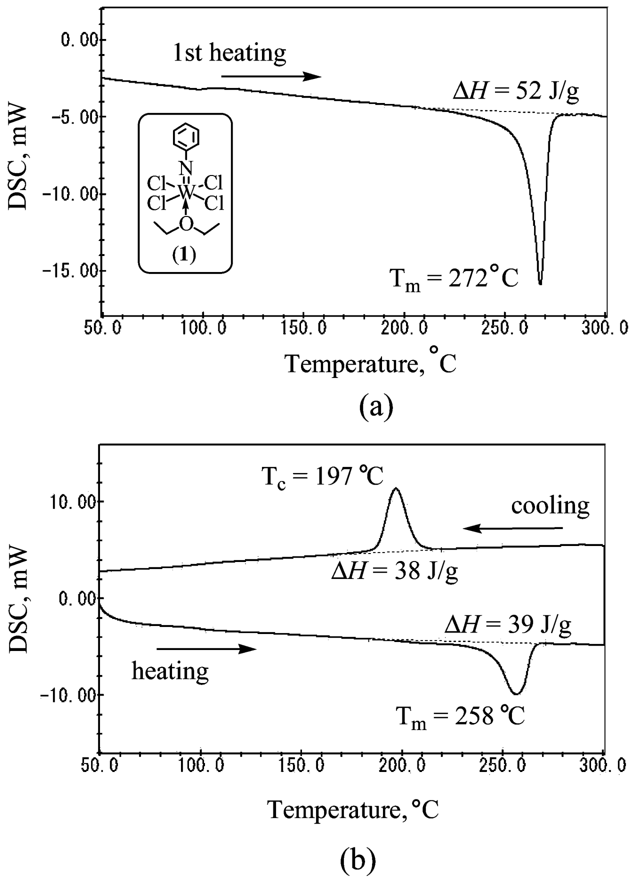


Figure 4. DSC thermograms of syndio-H-poly(DCPD) obtained from **1**-based catalyst (determined on the first heating scan for (a) and on the second scan for (b) under N_2 for 10 deg/min).

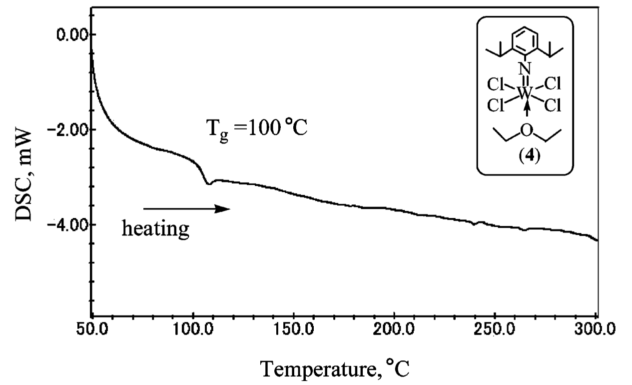


Figure 5. DSC thermograms of atactic H-poly(DCPD)s obtained by **4**-based catalyst (determined on the second scan under N_2 for 10 deg/min).

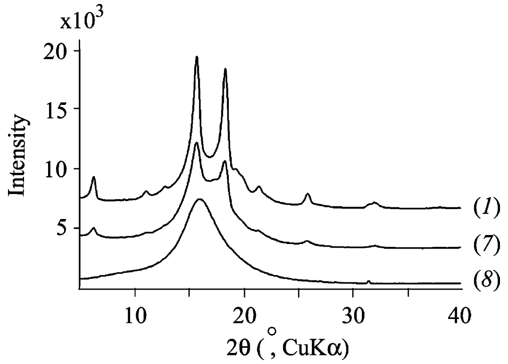


Figure 6. XRD patterns of H-poly(DCPD)s obtained from (*1*) W(=N−Ph)Cl_4·Et_2O (**1**), (*7*) W(=N−*n*-Hex)Cl_4·Et_2O (**7**), and (*8*) W(=N−cyclohexyl)Cl_4·Et_2O (**8**).

In conclusion, one can say that the present polymerization systems threw a new light on the possibility of the stereocontrol of ROMP. Great emphasis can be placed upon the fact that the syndiotacticity of the poly(DCPD) can be controlled in the range 30−80% by the suitable choice of the imido ligands.

Study on the Properties of the Hydrogenated Poly(DCPD)s: Development of Crystalline Syndiotactic H-poly(DCPD). The thermal properties of the poly(DCPD)s were investigated. As shown in Tables 2 and 3, all the poly(DCPD)s exhibited glass transition points at 140−160 °C. In contradiction to our expectation, *cis*- and syndiotactic poly(DCPD)s were amorphous and highly soluble. This feature is in sharp contrast to that of previous reported *cis*- and isotactic poly(DCPD)s, which were crystalline with melting point at 260 °C and entirely insoluble in ordinary solvents. It is interesting that the combination of *cis/trans* and m/r drastically affects the property of poly(DCPD)s.

Next, the hydrogenation of poly(DCPD)s was conducted, and the corresponding H-poly(DCPD)s were characterized by DSC. The DSC charts of the polymers obtained with **1** and **4** are shown in Figure 4 and Figure 5, respectively. It is worth noting that the fine powder of syndio-H-poly(DCPD), which was yielded by the sterically small catalysts **1** (and **5**), displayed a large endothermic peak at an elevated temperature on the first scan (Figure 4a for **1**). Further, the annealed syndio-H-poly(DCPD)s also possessed high melting point and large melting enthalpy, and rapid crystallization was also observed in the course of cooling (Figure 4b for **1**). These results clearly indicate that these syndio-H-poly(DCPD)s are crystalline polymers. *n*-Alkylimido catalysts **6** and **7** provided insoluble H-poly(DCPD)s whose syndiotacticity was only 70%. Despite their modest racemo ratio, DSC data suggested the crystalline nature of those H-poly(DCPD)s. The slightly syndiotactic H-poly(DCPD), which was produced by **2**, exhibited very small crystal fusing. When the racemo−dyad ratio diminished below 65%, H-poly(DCPD)s were revealed to become amorphous. The atactic H-poly(DCPD)s showed glass transition points at 100−105 °C (e.g., Figure 5 for **4**), as observed for the polymers formed with classic ROMP catalyst systems.[7,11]

The XRD study also implied the crystalline nature of syndio-H-poly(DCPD). Figure 6 depicted the XRD patterns of non-thermal history H-poly(DCPD)s obtained from (*1*) W(=N−Ph)Cl_4·Et_2O, (*7*) W(=N−*n*-Hex)Cl_4·Et_2O, and (*8*) W(=N-cyclohexyl)Cl_4·Et_2O. The XRD patterns of (*1*) and (*7*) were characteristic in sharp crystalline peaks, indicating that those H-poly(DCPD)s were crystalline polymers. **8** produced amorphous H-poly(DCPD); XRD pattern (*8*) showed only an amorphous halo. The weight fraction crystallinity (w_c) of syndio-H-poly(DCPD)s from **1** was evaluated by the separation of the crystalline peaks and the amorphous halo to be $w_c = 0.61$ (Figure 6).[21] The w_c of moderately syndio-biased H-poly(DCPD)s from **7** free of heat hysteresis was estimated to be about 0.30 and relatively high. It is interesting that the XRD patterns of (*1*) and (*7*) were supposed to be essentially identical, except for the intensity of the crystalline peaks. This result indicated that both samples possessed very similar crystal structures irrespective of their tacticity.

In conclusion, **1** and **5** turned out to be effective for the production of crystalline syndio-H-poly(DCPD)s. Those crystalline polymers exhibited relatively high crystallinity ($w_c = 0.61$).

Effects of Reaction Conditions. It is well-known that the *cis*/*trans* ratio and tacticity are often influenced by reaction

Table 4. Effects of Cocatalysts for the Polymerization of DCPD by $W(=N-Ph)Cl_4\cdot Et_2O$−Cocatalyst Systems[a]

cocatalysts	[W]:[cocat]	polymer yield, %	M_n[b]	M_w/M_n[b]	*cis*/*trans*	m/r[c]
none	1:0	no polymer				
$Et_2Al(OEt)$	1:1	85	13 400	2.6	92/8	20/80
$Et_2Al(OEt)$	1:2	100	11 400	2.8	92/8	20/80
$Et_2Al(OEt)$	1:3	100	10 100	3.5	93/7	20/80
$Et_2Al(OEt)$	1:10	100	11 200	3.0	92/8	20/80
Et_3Al	1:1	96	partially insoluble		89/11	
i-Bu_3Al	1:1	gelation				
n-Bu_4Sn	1:1	15	20 000	1.9	82/18	
n-BuLi	1:1	23	partially insoluble		92/8	

[a] Polymerized in cyclohexane at 50 °C for 3 h; [DCPD] = 1.3 M, [1-octene] = 50 mM, [W complex] = 1.3 mM, [$Et_2Al(OEt)$] = 3.6 mM. [b] Before hydrogenation. [c] Hydrogenated in cyclohexane at 160 °C for 8 h; [$Ru(Cy_3P)_2Cl_2(=CHOEt)$]/[DCPD unit] = 1/1000 in mol ratio, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa.

conditions, including cocatalysts, additives, solvents, polymerization temperature, and even monomer/catalyst ratio. Therefore, effects of reaction conditions were investigated on the polymerization of DCPD by catalyst **1** in more detail. The polymerization was carried out under the following conditions unless otherwise noted: in cyclohexane at 50 °C for 3 h; $[DCPD]_0 = 1.3$ M (20 wt %), [1-octene] = 50 mM, [**1**] = 1.3 mM.

The effect of the cocatalysts was examined in the polymerization of DCPD by $W(=N-Ph)Cl_4\cdot Et_2O$−cocatalyst (1:*x*) (Table 4). $W(=N-Ph)Cl_4\cdot Et_2O$ (**1**) alone exhibited no polymerization activity. $Et_2Al(OEt)$ was verified to be useful as a cocatalyst of $W(=N-Ph)Cl_4\cdot Et_2O$. When an equimolar of $Et_2Al(OEt)$ was added to $W(=N-Ph)Cl_4\cdot Et_2O$, polymerization was induced to form some extent of syndiotactic poly(DCPD). However, catalyst aging of 15 min did not turn the green catalyst solution into brown, implying an equimolar of $Et_2Al(OEt)$ was insufficient to activate all of $W(=N-Ph)Cl_4\cdot Et_2O$. On the other hand, when 2 equiv or more of $Et_2Al(OEt)$ was employed, catalyst aging proceeded smoothly to provide syndiotactic poly(DCPD)s in quantitative yields. These results indicate that the 2 equiv of $Et_2Al(OEt)$ was the minimum quantity to activate the W−imido catalyst effectively, and the excess amount of $Et_2Al(OEt)$ did not affect the polymerization nature. Moreover, it was found that the addition of the 3-fold of $Et_2Al(OEt)$ seems favorable and adequate from the viewpoint of polymerization reproducibility. The $W(=N-Ph)Cl_4\cdot Et_2O-Et_3Al$ also promoted the rapid polymerization of DCPD, whereas the obtained poly(DCPD) was contaminated by an insoluble poly(DCPD), suggesting side reactions. When *i*-Bu_3Al was employed as a cocatalyst, the DCPD polymerization ended in gelation. The *n*-Bu_4Sn was found to be ineffective as a cocatalyst because polymerization was very sluggish. The use of *n*-BuLi afforded small amounts of the mixture of soluble poly(DCPD) and insoluble polymer. Thus, $Et_2Al(OEt)$ turned out to be the most effective cocatalyst to promote syndioselective ROMP without any side reaction, and the 3-fold use of $Et_2Al(OEt)$ seems to be more favorable. Unfortunately, the exact nature of the propagating species is still unknown in the present $W(=N-Ph)Cl_4\cdot Et_2O-Et_2Al(OEt)$ binary catalyst. We can only speculate as follows: Reaction of $W(=N-Ph)Cl_4\cdot Et_2O$ (**1**) with $Et_2Al(OEt)$ generated a dialkyl species $(C_2H_5)_2W(=N-Ph)Cl_2$. Then the ethyl group on the W presumably becomes an ethylidene by α-H elimination. The above-stated tungsten ethylidene [$(CH_3CH=)W(=N-Ph)Cl_2$] would be the initiating species of the present syndioselective polymerization.[22]

The effect of the polymerization temperature was examined. In general, stereospecificity of the polymerization would increase with the dropping of the polymerization temperature, owing to the decrease of stereoerror. Thus, the polymerization temperature was changed to determine the effect upon the stereochemistry of the present syndioselective polymerization. At 0 °C, the polymerization became very slow; polymer yield was 20% after 24 h of the polymerization. The polymer yield at 25 °C was 76% for 24 h polymerization. At 60 °C, the polymerization ended instantaneously to form poly(DCPD) in a quantitative yield. In contradiction to our expectations, the steric structures of these obtained polymers were essentially identical: *cis* = 93%, m/r = 20/80, and the thermal property of each H-poly(DCPD) was almost the same. This implies that the reaction temperature did not largely affect the stereochemistry of the enchainment reaction in the range 0−60 °C.

It is generally recognized that solvents and basic additives sometimes interact with propagation species to change the polymerization nature drastically. Hence, the effect of polymerization solvents/additives was investigated for the purpose of enhancing the syndiotacticity of H-poly(DCPD). When toluene was employed as polymerization solvent, polymerization proceeded smoothly to yield *cis*- and syndiotactic poly(DCPD). The syndiotacticity of its hydrogenated product was identical to that polymerized in cyclohexane. We have also carried out the polymerization in $CHCl_3$ as a noncoordinating solvent. The DCPD polymerization proceeded in a manner similar to form the essentially identical polymer. THF, which is regarded as polar solvent, was examined for polymerization solvent next. The employment of THF decelerated the polymerization (at 50 °C for 3 h, polymer yield 80%). However, the stereostructure of the corresponding poly(DCPD) did not change. Furthermore, it was proven that the basic additives such as PPh_3 and pyridine only retarded the polymerization. Contrary to our expectation, it can be concluded that neither *cis*/*trans* nor tacticity was dependent on the solvents/additives employed.

Summary

The present study is summarized as follows: Tungsten complexes, $W(=N-Ph)Cl_4\cdot Et_2O$ and $W(=N-Et)Cl_4\cdot Et_2O$, realized *cis*- and syndioselective ROMP of DCPD (*cis* > 90% and r > 80%). The syndioselectivity of the ROMP could be controlled by the suitable choice of tungsten imido catalysts. The new crystalline polymer, crystalline syndio-H-poly(DCPD), was developed on the basis of the present catalyst systems. We hope that the present new catalysts may expand the utility of stereoselective ROMP and related metathesis reaction.

Acknowledgment. The authors thank Prof. Takeshi Shiono, Prof. Yuushou Nakayama, Dr. Hideaki Iwatani, Dr. Mikio Yamasaki, and Dr. Motoo Shiro for their helpful discussions.

Supporting Information Available: ^1H and ^{13}C NMR charts of the poly(DCPD) and the H-poly(DCPD), the determination of degree of crystallinity, and the detail of single-crystal X-ray diffraction measurement (experimental details, final positional parameters, final thermal parameters, bond distances, and angles) for **1** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) On the basis of ^{1}H NMR study, we have found that the degree of polymerization of the poly(DCPD) could be estimated using the integration ratio of main chain peaks/chain transfer end peak (i.e., the *n*-C_6 of 1-octene) (Figure S-2). One can say that the M_n(GPC) was relatively similar to M_n(NMR). Unfortunately, we had no information on whether all the poly(DCPD) chain possessed one chain-transfer end or not. In addition, we felt that the ^{1}H NMR method was not accurate enough to determine the molecular weight because the molecular weight of the present polymers was rather high. Therefore, we have decided to employ high-temperature GPC instead of ^{1}H NMR for the estimation of molecular weight.

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(20) On the basis of our knowledge, low-*cis* poly(DCPD)s have a tendency to be less soluble in ordinary solvents.

(21) Crystallinity of crystalline H-poly(DCPD) was estimated by XRD as follows: At first, the films of syndio-H-poly(DCPD) was prepared by compression-molding just above its melting point. The film was quench-cooled by liquid N_2 in order not to proceed the crystallization. The amorphous halo was determined using a complete amorphous syndio-H-poly(DCPD) film stated above. Then, the XRD pattern of crystalline syndio-H-poly(DCPD) without heat history was recorded. Reflections owing to crystalline region were separated from halo of amorphous region, and the crystallinity was calculated using crystalline/amorphous area ratio. XRD charts of (i) the powder without heat hysteresis and (ii) the quench-cooled film of the syndio-H-poly(DCPD) are available in the Supporting Information (Figure S-4).

(22) To gain the information about the active species, we have conducted the ^{1}H NMR measurement of $W(=N-Ph)Cl_4\cdot Et_2O-Et_2Al(OEt)$ prepared in situ. The ^{1}H NMR spectrum revealed a broad signal at $\delta = 11.60$ ppm, which would be attributed to the α-protons of the carbene species, while strong signals of the ethyl group were also observed at $\delta = 0.83$ ppm (brs, 3H, CH_3) and 0.10 ppm (brs, 2H, CH_2), indicating the presence of W-Et species. These facts supported the formation of W−ethylidene by α-H elimination of ethyl group on the tungsten. However, it was not clarified whether these carbene species are initiating species or not. Moreover, the exact initiation efficiency could not be estimated since the intensity of the α-proton signal varied with aging time and temperature. At least, we can report that the average value of the initiation efficiency was about 2% based on the integration (α-proton of carbene species/aromatic proton in ^{1}H NMR). Unfortunately, exact nature of the propagating species has been still unknown in the present $W(=N-Ph)Cl_4\cdot Et_2O-Et_2Al(OEt)$ binary catalyst.

MA052088C