Stereospecific Ring-Opening Metathesis Polymerization of Cycloolefins Using Novel Molybdenum and Tungsten Complexes Having Biphenolate Ligands. Development of Crystalline Hydrogenated Poly(*endo*-dicyclopentadiene) and Poly(norbornene)

Shigetaka Hayano,[†] Hiroshi Kurakata,[†] Yasuo Tsunogae,*[,†] Yuushou Nakayama,[‡] Yoshinori Sato,[‡] and Hajime Yasuda*[,‡]

Zeon Corporation, 1-2-1 Yako, Kawasaki-ku, Kawasaki 210-9507, Japan, and Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Received May 12, 2003; Revised Manuscript Received August 6, 2003

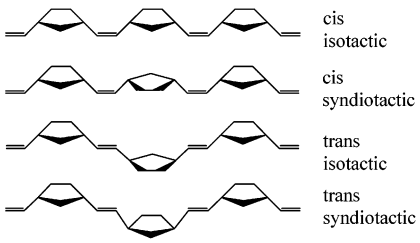
ABSTRACT: Novel molybdenum- and tungsten-based catalysts induced stereospecific ring-opening metathesis polymerization (ROMP) of cycloolefins to produce a new class of crystalline polymers. Various monomeric molybdenum(VI) and tungsten(VI) complexes of the general formula $M(=O)(O-Ar)_4$ (M = Mo or W; $(O-Ar)_4$ is two biphenolate or four phenolate ligands) were prepared. These catalysts exhibited moderate ROMP activity in the presence of cocatalyst such as *n*-BuLi and Et_3Al. The molybdenum and tungsten complexes bearing substituted biphenolate ligands such as oxomolybdenum(VI) bis(*racemic*-5,5′,6,6′-tertamethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diolate) promoted cis and isospecific ROMP of *endo*-dicyclopentadiene (cis > 90% and meso > 95%). The novel ternary and quarternary catalysts such as $MoOCl_4$−biphenolate−*n*-BuLi (1:2:2) were developed as a new useful methodology to control the stereoselectivity of the ROMP. Hydrogenation of the cis-isotactic poly(*endo*-dicyclopentadiene)s and poly(norbornene)s provided novel crystalline polymers with high melting points (295 °C, ΔH = 50 J/g; 175 °C, ΔH = 60 J/g, respectively), which can be regarded as a new class of crystalline polymers.

Introduction

In recent years, precise polymerization has been researched extensively in order to develop new, versatile polymeric materials. Especially, transition-metal-catalyzed polymerization has been an effective means to accomplish precise polymerizations, such as stereospecific polymerizations and living polymerizations. For instance, the research on metallocene and nonmetallocene catalysts of early transition metals has made great advancement over the past two decades. Consequently, the appropriate molecular design of these catalysts has resulted in the stereospecific and/or living polymerizations of olefins and polar monomers.[1] On the basis of these studies, it is recognized that the precise control of stereoregularity of the polymer backbone changes the physical properties in the conventional polymeric materials (e.g., syndiotactic polystyrene, syndiotactic polypropylene).[1,2]

It is also well-known that the development of metal carbene complexes (e.g., Mo carbenes and Ru carbenes) and several related catalysts (Ti, V, Ta, W, and Re complexes) have also enabled the precise polymerization of cycloolefins in the field of ring-opening metathesis polymerization (ROMP).[3−8] Molybdenum (and tungsten) imidoalkylidene complexes, i.e., Schrock catalysts and Schrock−Hoveyda catalysts, have made extensive progress with ROMP and several types of olefin metathesis reactions.[5] An extensive number of superior ruthenium carbenes (Grubbs' catalysts) have been developed. The main characteristics are extremely high catalyst activity and high tolerance against polar functional groups in the monomer and solvent.[6]

Scheme 1. Four Possible Structure of Poly(norbornene)



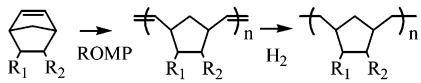
To date, there has been vigorous study of the stereocontrol of ROMP. In the case of poly(norbornene), there are four possible structures in the polymer backbone (i.e., cis/trans and meso/racemo) (Scheme 1). The stereospecific ROMP of several cycloolefins (e.g., 2,3-bis(trifluoromethyl)norbornene) has been investigated in detail.[7a−e] Schrock−Hoveyda catalysts, which possess diolate ligand, were especially useful in controlling the stereochemistry of ROMP. Recently, it was reported that chiral Schrock−Hoveyda catalysts are useful for asymmetric ring-closing metathesis (ARCM) and have been gathering some attention as a powerful tool for organic synthesis.[5c,d,7f−j] To the best of our knowledge, the appropriate design of chiral diolate ligands resulted in the catalyst's high utility for ARCM. Then it may be said that both stereospecific ROMP and ARCM have been developed on the basis of the investigation and insight into the asymmetric metathesis reaction.

Synthesis and characterization of various poly(cycloolefin)s and its hydrogenated products have been studied in the past.[8] In general, hydrogenated poly(cycloolefin)s are prepared by ROMP of cycloolefins followed by hydrogenation of double bonds (Scheme 2). Most of the hydrogenated poly(cycloolefin)s are amorphous plas-

[†] Zeon Corporation.
[‡] Hiroshima University.

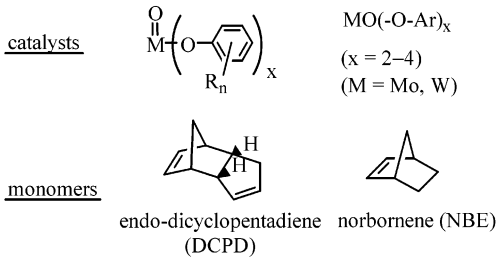
10.1021/ma034611y CCC: $25.00
Published on Web 08/29/2003

Scheme 2. Preparation of Hydrogenated Poly(cycloolefin)s



(R_1, R_2: H or functional groups)

Scheme 3. Catalysts and Monomers in This Study



tic when its main chain is atactic. On the contrary, we have already reported that the Schrock−Hoveyda catalyst provided the crystalline hydrogenated poly(*endo*-dicyclopentadiene) (T_m = 290 °C, ΔH = 42 J/g), a backbone which is supposed to be isotactic.[9] On the basis of the above stated point, the diolate ligand appears to be the key ligand that controls the stereochemistry in the metathesis reaction.

This viewpoint leads to investigate the isospecific ROMP of several polycyclic olefins, followed by the hydrogenation of the resultant polymers with the intention of developing a new class of highly crystalline polymers having rigid ring structures in the main chain. The research has focused on the polymerization of *endo*-dicyclopentadiene (DCPD) and norbornene (NBE) using the novel molybdenum(VI) and tungsten(VI) phenolate type complexes such as oxomolybdenum(VI) bis(*racemic*-5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diolate) (Scheme 3). This article reports a novel methodology to produce highly crystalline hydrogenated poly(DCPD) and poly(NBE), both of which appeared to be a new class of crystalline polymers.[9]

Experimental Section

General Remarks. All operations were carried out under a dry argon atmosphere by using standard Schlenk techniques. $MoOCl_4$ (Strem), WCl_6 (Soegawa Chemical), Et_3Al (Kanto Chemical), MeMgI (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 according to the literature.[10] Ni(II) acetate anhydrous ($Ni(OAc)_2$) was prepared by dehydration of Ni(II) acetate tetrahydrate. Grubbs catalyst, $Ru(Cy_3P)_2Cl_2$(=CHPh) (Strem), was used as received. *n*-Hexane and diethyl ether as reaction solvents were distilled over sodium−potassium alloy under an argon atmosphere before use. Toluene and cyclohexane were purified by distillation over sodium metal. Methylene chloride was distilled over calcium hydride. Hexamethyldisiloxane was distilled over molecular sieves under reduced pressure. Commercially available (*R*)-(+)-5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol (*R*)-(+)-biphenol, (*R*)-(+)-biphenH_2) (Strem), *racemic*-5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol (*rac*-biphenol, *rac*-biphenH_2) (Strem), 3,3′,5,5′-tetramethyl-2,2′-biphenol (Strem), (*S*)-(−)-4,5-bis[hydroxy(diphenyl)-methyl]-2,2′-dimethyl-1,3-dioxolane ((*S*)-(−)-taddol) (Tokyo Kasei), 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (Wako Chemicals), (*R*)-(+)-2,2′-bi-1,1′-naphthol (Tokyo Kasei), and 2,6-dimethylphenol (Wako Chemicals) were used as received. *endo*-Dicyclopentadiene (DCPD) (Zeon Corp.) and norbornene (NBE) (Wako Chemicals) were distilled over calcium hydride under reduced pressure and stored as cyclohexane solution. 1-Octene (Wako Chemicals) was distilled over calcium hydride.

MoO((*R*)-(+)-biphenolate)$_2$·C_7H_8·C_6H_{14} (1). Dilithium (*R*)-(+)-biphenolate (4.19 g, 11.82 mmol) in diethyl ether (30 mL) was dropwise added to a solution of $MoOCl_4$ (1.50 g, 5.91 mmol) in diethyl ether (30 mL) at −78 °C. The mixture was allowed to warm to ambient temperature. The reaction mixture was stirred for 18 h to give a dark-blue solution. Diethyl ether was removed in vacuo, and the residue was extracted with toluene. The blue extract was dried in vacuo to yield the desired product as a deep-blue powder in 96% yield. Recrystallization from toluene/*n*-hexane gave deep-blue needle crystals of MoO((*R*)-(+)-biphenolate)$_2$·C_7H_8·C_6H_{14} (**1**). Two crops of corresponding crystals were collected by filtration and dried in vacuo (yield 53% (2.56 g, 3.13 mmol)). An analytically pure sample was obtained by repeated recrystallization from toluene/*n*-hexane. ^{1}H NMR (C_6D_6): δ 7.24 (s, 1, H_{aryl}), 7.19 (s, 1H, H_{aryl}), 7.13−7.02 (m, 5H, toluene), 2.13 (s, 3H, CH_3), 2.11 (s, 3H, toluene), 2.03 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.52 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu), 1.24 (m, 8H, *n*-hexane), 0.89 (t, 6H, *n*-hexane). EI-MS for ^{98}Mo, m/z = 818 (M^+). Anal. Calcd for $MoC_{48}H_{64}O_5$·C_7H_8·C_6H_{14}: C, 73.61; H, 8.71. Found: C, 73.84; H, 8.68. Melting point (T_m): 200 °C.

MoO(*rac*-biphenolate)$_2$·C_7H_8 (2). This complex was prepared and isolated in the same manner as described in the catalyst **1** synthesis section. The desired product was a deep-blue powder with 93% yield. Recrystallization from toluene/*n*-hexane gave deep-blue prism crystals of MoO(*rac*-biphenolate)$_2$·C_7H_8 (**2**). The corresponding crystals were collected in three crops by filtration and dried in vacuo (yield 69%). ^{1}H NMR (C_6D_6): δ 7.24 (s, 1, H_{aryl}), 7.19 (s, 1H, H_{aryl}), 7.13−7.02 (m, 5H, toluene), 2.13 (s, 3H, CH_3), 2.11 (s, 3H, toluene), 2.03 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.52 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu). EI-MS for ^{98}Mo, m/z = 818 (M^+). Anal. Calcd for $MoC_{48}H_{64}O_5$·C_7H_8: C, 72.66; H, 7.98. Found: C, 72.14; H, 8.02. T_m: 199 °C.

WO(*rac*-biphenolate)$_2$ (3). This complex was prepared and isolated in essentially the same manner as described in the catalyst **1** synthesis section. The desired product was a deep-red powder in 96% yield. Recrystallization from pentane gave deep-red prism crystals of WO(*rac*-biphenolate)$_2$ (**3**). Two crops of corresponding crystals were collected by filtration and dried in vacuo (yield 14%). An analytically pure sample was obtained by repeated recrystallization from pentane. ^{1}H NMR (C_6D_6): δ 7.36 (s, 1H, H_{aryl}), 7.27 (s, 1H, H_{aryl}), 2.14 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.56 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu). EI-MS for ^{184}W, m/z = 904 (M^+). Anal. Calcd for $WC_{48}H_{64}O_5$: C, 63.71; H, 7.13. Found: C, 63.96; H, 7.05. T_m: 220 °C.

MoO(3,3′,5,5′-Me_4-biphenolate)$_2$ (4). This complex was prepared and isolated in a manner similar to that in the catalyst **1** synthesis section. The expected product was a black powder in 83% yield. Recrystallization from toluene/*n*-hexane gave a black powder of MoO(3,3′,5,5′-Me_4-biphenolate)$_2$ (**4**). The corresponding powder was collected in two crops by filtration and dried in vacuo (yield 45%). An analytically pure sample was obtained by repeated recrystallization from toluene/*n*-hexane. EI-MS for ^{98}Mo, m/z = 594 (M^+). Anal. Calcd for $MoC_{32}H_{32}O_5$: C, 64.86; H, 5.44. Found: C, 65.03; H, 5.58. T_m: 229 °C.

MoO[2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)]$_2$ (5). This complex was isolated in the same method as described in the catalyst **1** synthesis section to yield a desired product as a deep-blue powder in 95% yield. Recrystallization from toluene/*n*-hexane gave a deep-blue needle microcrystals of MoO[2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)]$_2$ (**5**). The corresponding microcrystals were collected by filtration and dried in vacuo (yield 33%). An analytically pure sample was obtained by repeated recrystallization from toluene/*n*-hexane. ^{1}H NMR (C_6D_6): δ 6.89 (d, 2H, H_{aryl}), 6.74 (d, 2H, H_{aryl}), 5.74 (d, 1H, CH_2), 3.35 (d, 1H, CH_2), 2.04 (s, 6H, Me), 1.52 (s, 18H, *t*-Bu). EI-MS for ^{98}Mo, m/z = 790 (M^+). Anal. Calcd for $MoC_{46}H_{60}O_5$: C, 70.76; H, 6.71. Found: C, 70.11; H, 7.45. T_m: 120 °C (dec).

MoO((*S*)-(−)-taddolate)$_2$·C_7H_8 (6). This complex was prepared and isolated in a manner similar to that in the catalyst **1** synthesis section. The desired product was a yellow powder in a yield of 75%. Recrystallization from toluene/*n*-hexane gave a yellow needle microcrystals of MoO((*S*)-(−)-taddolate)$_2$·C_7H_8 (**6**). Two crops of the corresponding powder were collected by filtration and dried in vacuo (yield 18%). ^{1}H NMR (C_6D_6): δ 7.97 (m, 4H, H_{aryl}), 7.63 (m, 4H, H_{aryl}), 7.18 (m, 12H, H_{aryl}), 7.13−7.02 (m, 5H, toluene), 5.57 (d, 1H, CH), 5.40 (d, 1H, CH), 2.11 (s, 3H, toluene), 0.75 (d, 6H, Me). EI-MS for ^{98}Mo, m/z = 968 ((M − $C_3H_6O_2$)$^+$) and 74 ($C_3H_6O_2^+$). Anal. Calcd for $MoC_{62}H_{56}O_9$·C_7H_8: C, 73.13; H, 5.69. Found: C, 72.34; H, 5.44. T_m: 152 °C.

MoO((*R*)-(+)-binaphtholate)$_2$ (7). This complex was prepared in the same manner as described in the catalyst **1** synthesis section to yield a desired product as a dark-brown powder in 71% yield. Recrystallization from toluene/*n*-hexane gave a dark-brown powder of MoO((*R*)-(+)-binaphtholate)$_2$ (**7**). The corresponding powder was collected in three crops by filtration and dried in vacuo (yield 27%). ^{1}H NMR (C_6D_6): δ 9.3−6.5 (brs, H_{aryl}). Anal. Calcd for $MoC_{40}H_{24}O_5$: C, 70.59; H, 3.55. Found: C, 70.79; H, 4.23. T_m: 230 °C.

MoO(2,6-Me$_2$-phenolate)$_4$ (8). Lithium 2,6-dimethylphenolate (4.97 g, 38.8 mmol) in diethyl ether (50 mL) was dropwise added to a solution of $MoOCl_4$ (2.46 g, 9.70 mmol) in diethyl ether (50 mL) at −78 °C. The mixture was allowed to warm to ambient temperature. The reaction mixture was stirred for 18 h to give a dark-blue solution. Diethyl ether was removed in vacuo, and the residue was extracted with toluene. The blue extract was dried in vacuo to yield the desired product as a deep-blue powder in 74% yield. Recrystallization was performed from toluene/*n*-hexane to give deep-blue needle crystals of MoO(2,6-Me$_2$-phenolate)$_4$ (**8**). The corresponding needle crystals were collected by filtration and dried in vacuo (yield 23% (1.33 g, 2.23 mmol)). ^{1}H NMR (C_6D_6): δ 6.71 (d, 2H, H_{aryl}), 6.57 (t, 1H, H_{aryl}), 2.36 (d, 6H, CH_3). EI-MS for ^{98}Mo, m/z = 598 (M^+). Anal. Calcd for $MoC_{32}H_{36}O_5$: C, 64.43; H, 6.08. Found: C, 63.69; H, 6.69. T_m: 192 °C.

WO(2,6-Me$_2$-phenolate)$_4$ (9). This complex was prepared in the same manner as described in the catalyst **8** synthesis section. The desired product was a reddish-brown powder in 76% yield. Recrystallization from toluene/*n*-hexane gave a reddish-brown needle crystals of WO(2,6-Me$_2$-phenolate)$_4$ (**9**). The corresponding crystals were collected by filtration and dried in vacuo (yield 20%). ^{1}H NMR (C_6D_6): δ 6.75 (d, 2H, H_{aryl}), 6.58 (t, 1H, H_{aryl}), 2.35 (s, 6H, Me). EI-MS for ^{184}W, m/z = 684 (M^+). Anal. Calcd for $WC_{32}H_{36}O_5$: C, 56.15; H, 5.30. Found: C, 56.17; H, 5.30. T_m: 218 °C.

Analyses of Complex and Polymer. ^{1}H NMR spectra were recorded on a Bruker AMX 400web spectrometer (400.13 MHz), and chemical shifts were calibrated using the residual benzene protons (δ 7.16 ppm) or tetramethylsilane (δ 0.00 ppm). ^{13}C NMR spectra were measured on a JEOL JNM-EX400WB spectrometer (100.53 MHz for ^{13}C), and chemical shifts were determined with reference to *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. EI-MS spectra were recorded on a JEOL JMS-SX-102A spectrometer. 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 Seiko model SSC/5200 DSC220 in a dry nitrogen stream. Crystallinity of the polymers was estimated on X-ray diffractometer (XRD) (Rigaku RINT 2500).

Polymerization. Polymerization was carried out in a prebaked ampule tube equipped with a rubber septum at 80 °C. Polymerization catalyst solutions were prepared as follows unless otherwise stated: A toluene solution of MoO(*rac*-biphenolate)$_2$ (**2**) (0.0515 g, 56.7 μmol) was mixed with 2 equiv of *n*-BuLi at −78 °C, and the mixture (deep-blue solution) was allowed to warm to ambient temperature. The mixture was aged for an additional 15 min, resulting in becoming a reddish-orange solution. A cyclohexane solution of DCPD (7.50 g, 56.7 mmol) and 1-octene (0.127 g, 1.13 mmol) was added to the mixture at the prescribed temperature. After stirring for a fixed time, the polymerization was quenched with a small amount of 2-propanol. The polymer yield was determined by gravimetric measurement.

Table 1. Crystal Parameters of MoO((*R*)-(+)-biphenolate)$_2$·C_7H_8·C_6H_{14} (1) and MoO(O−Me$_2$Ph)$_4$ (8)

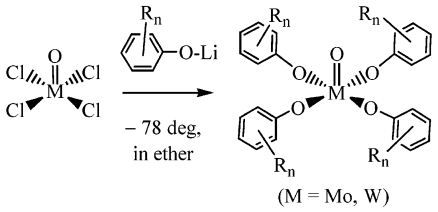
parameter	**1**	**8**
chem formula	$C_{48}H_{64}MoO_5$·C_7H_8·C_6H_{14}	$C_{32}H_{36}MoO_5$
FW	995.29	596.57
color	black	black
crystal system	monoclinic	tetragonal
lattice params		
a, Å	10.1622(7)	14.028(1)
b, Å	18.344(1)	14.028(1)
c, Å	15.001(1)	7.3532(6)
α, deg	90	90
β, deg	93.902(3)	90
γ, deg	90	90
V, Å^3	2789.9(3)	1446.9(2)
space group	$P2_1$	$P4/n$
Z	2	2
D_{calc}, g/cm^3	1.185	1.369
μ(Mo Kα), cm^{-1}	2.80	4.90
$2\theta_{max}$, deg	55.0	55.0
oscillation range		
(ϕ = 0.0°, χ = 45.0°)	ω 130.0−190.0° with 5.0° step	
(ϕ = 180.0°, χ = 45.0°)	ω 0.0−160.0° with 5.0° step	
no. of reflections	total: 24 138 unique: 6564 (R_{int} = 0.046)	total: 11 269 unique: 1672 (R_{int} = 0.043)
no. of observations	6545 ((all, 2σ < 54.95°))	1672 ($I > 0.00\sigma(I)$)
no. of variables	540	98
goodness-of-fit on F^2	1.07	1.17
R_1 (all data)[a]	0.050	0.042
R_w (all data)[b]	0.164	0.109

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)]^{1/2}$; $w = 1/[\sigma^2(Fo^2)]$.

Hydrogenation. A cyclohexane slurry of poly(DCPD) and a cyclohexane solution of hydrogenation catalyst (Ru- or Ni-based 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. The Ni-based hydrogenation catalyst solutions were prepared as follows: A cyclohexane slurry of Ni(OAc)$_2$ was mixed with 4-fold of Al(*i*-Bu)$_3$ at ambient temperature, and the mixture was allowed to heat to 60 °C. The mixture was aged for an additional 30 min, and the resultant slurry turned to a black solution, indicating the formation of reduced Ni(0) species. Ru-based hydrogenation catalyst solutions were prepared as follows: Ru(Cy$_3$P)$_2$Cl$_2$(=CHOEt), the precursor of hydrogenation catalyst, was prepared from Ru(Cy$_3$P)$_2$Cl$_2$(=CHPh) and 50-fold excess of ethyl vinyl ether.[11] 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 possible becoming an active species of hydrogenation.[11]

X-ray Structure Determination of 1 and 8. Single crystals of **1** and **8** suitable for X-ray diffraction sealed in a glass capillary under an argon atmosphere were 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 −93 °C. Indexing was performed for three oscillations, which were exposed for 3.0 min. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A numerical absorption collection using

Scheme 4. Synthesis of Mo (and W) Aryloxo Complexes



the program NUMABS[12a] was applied for **1**, whereas a correction for secondary extinction[12b] was applied for **8** (coefficient = 608.450 012). The data were corrected for Lorentz and polarization effects. The structures of **1** and **8** were solved by direct methods (SHELXS-97[13a] for **1**, SIR92[13b] for **8**) and expanded using Fourier techniques (DIRDIF94[14a] for **1**, DIRDIF99[14b] for **8**). In the final refinement cycle (full-matrix), hydrogen atom locations were included at an idealized position, and the hydrogen atoms were given in the same temperature factor as that of carbon atoms to which they were bonded. All non-hydrogen atoms other than crystalline solvents were anisotropically refined, while the crystalline solvents were refined isotropically. All calculations were performed using the teXsan or Crystal Structure 3.10 crystallographic software package.

Results and Discussion

Synthesis of Oxo Complexes of Molybdenum and Tungsten Having Biphenolate Ligands. To date, syntheses and ROMP catalyses of molybdenum and tungsten phenolate (and alkoxide) type complexes have already been studied in detail.[15] To our knowledge, WCl_6, $WOCl_4$, $MoOCl_4$, and $W(=NAr)Cl_4$ seem to be the typical starting materials. These can be easily transformed into phenolate and alkoxide complexes. In general, tungsten-based complexes were more widely reported than molybdenum-based complexes. Typical examples for W-based complexes are as follows: $W(OAr)_3Cl_3$,[15a] $W(OAr)_4Cl_2$,[15a,b] $W(OAr)_6$,[15c] $WO(OAr)_2Cl_2$,[15d] $WO(OAr)_4$,[15d] $WO(OR)_4$,[15e] $W(=NAr')(OAr)_2Cl_2$,[15f] $W(=NAr')(OAr)_4$,[15f] and $W(=NAr')(OR)_4$.[15g] Lithium or sodium phenolates and phenols themselves have been mostly employed for the ligand exchange reaction to synthesize above-stated W complexes. On the other hand, the use of aryltrimethylsilyl ethers ($Me_3Si-O-Ar$) is convenient to prepare mono- and bis(phenolate) complexes.[15h] It is also reported that tungsten(VI) tris(1,2-ethanediolate) and molybdenum(VI) bis(acetylacetonate) dioxide are versatile precursors to synthesize phenolate or binaphtholate complexes.[15i–k] In this case the phenols themselves were used for the alkoxide displacement reaction.

In this study, $MoOCl_4$ and $WOCl_4$ were selected as starting materials, and lithium salts were employed as ligand exchange reagents for the purpose of producing $M(=O)(O-Ar)_4$ (M = Mo or W; $(O-Ar)_4$ is two biphenolate or four phenolate ligands). $MoOCl_4$ and $WOCl_4$ were treated with 2-fold of bidentate dilithium biphenolates or 4-fold of monodentate lithium phenolates in diethyl ether at low temperature, and the crude products of $M(=O)(O-Ar)_4$, which were pure enough for use, were obtained in moderate yields (Scheme 4). These products could be recrystallized from suitable solvents such as toluene/*n*-hexane to yield highly pure products. Then the following complexes were prepared: MoO((*R*)-(+)-biphenolate)$_2$ (**1**), MoO(*rac*-biphenolate)$_2$ (**2**), WO(*rac*-biphenolate)$_2$ (**3**), MoO(3,3′,5,5′-Me_4-biphenolate)$_2$ (**4**), MoO[2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)]$_2$ (**5**), MoO((*S*)-(−)-taddolate)$_2$ (**6**), MoO((*R*)-(+)-binaphtholate)$_2$ (**7**), MoO(2,6-Me_2-phenolate)$_4$ (**8**), and WO(2,6-Me_2-phenolate)$_4$ (**9**) (Scheme 5). ^{1}H NMR, elemental analysis, EI-MS, and melting point measurement identified these complexes. The ^{1}H NMR spectra of the complexes **1** and **2** were completely identical, indicating that the complex **2** consisted of racemic diastereomers, MoO((*R*)-(+)-biphenolate)$_2$ (**1**) and MoO((*S*)-(−)-biphenolate)$_2$, and did not contain a meso isomer, MoO((*R*)-(+)-biphenolate) ((*S*)-(−)-biphenolate).

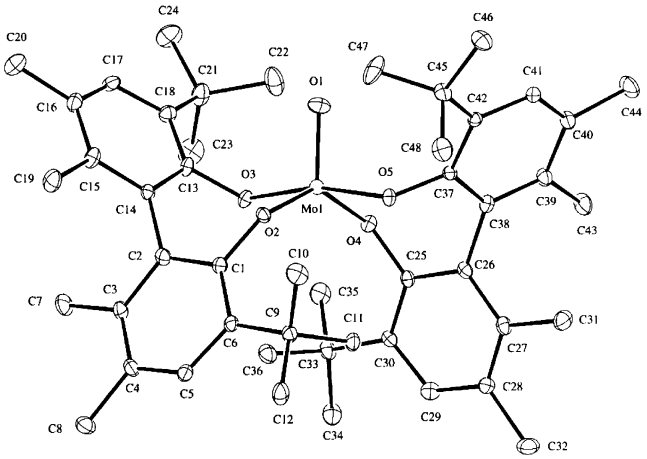
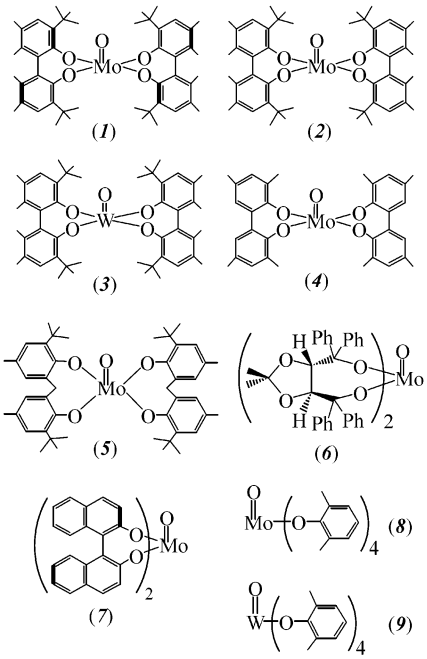


Figure 1. ORTEP representation of MoO((*R*)-(+)-biphenolate)$_2$ (**1**).

Scheme 5. Mo (and W) Aryloxo Complexes



Single-crystal X-ray diffraction studies on MoO((*R*)-(+)-biphenolate)$_2$ (**1**) and MoO(2,6-Me_2-phenolate)$_4$ (**8**) were carried out, and their molecular structures are shown in Figures 1 and 2, respectively. Selected bond lengths and angles are also shown in Table 2. Complex **1**, which appears to have a crystallographic C_2 axis through Mo and O1, has distorted square-pyramidal geometry with the terminal oxo ligand in the apical position. The C(1)−C(2)−C(14)−C(13) torsion angle of the (*R*)-(+)-biphenolate group of **1** (69.4(7)°) is significantly narrower than that of Schrock−Hoveyda catalyst (102°).[7i] The bond length between Mo and terminal oxo group (O1) is 1.672(4) Å. The geometry of **1** is somewhat

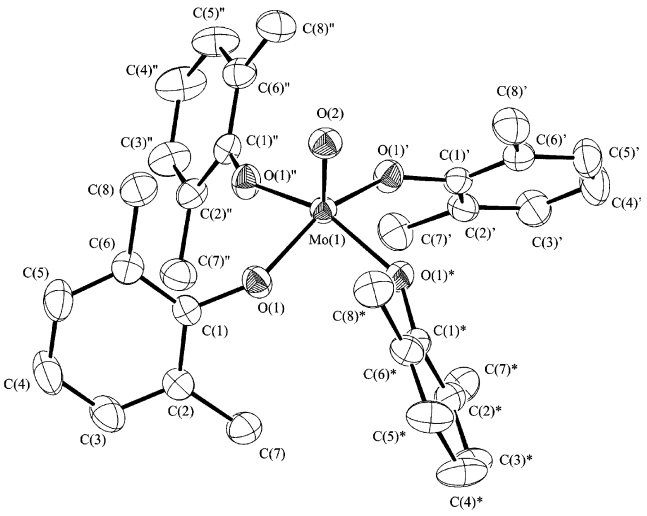


Figure 2. ORTEP drawing of MoO(O-Me_2Ph)$_4$ (**8**).

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for MoO((*R*)-(+)-biphenolate)$_2$·C_7H_8·C_6H_{14} (1) and MoO(O−Me_2Ph)$_4$ (8)

MoO((*R*)-(+)-biphenolate)$_2$·C_7H_8·C_6H_{14} (**1**)			
Mo−O(1)	1.672(4)	Mo−O(2)	1.881(4)
Mo−O(3)	1.937(4)	Mo−O(4)	1.895(3)
Mo−O(5)	1.928(4)		
O(1)−Mo−O(2)	110.7(2)	O(1)−Mo−O(3)	97.3(2)
O(1)−Mo−O(4)	110.7(2)	O(1)−Mo−O(5)	96.7(2)
O(2)−Mo−O(4)	138.6(2)	O(3)−Mo−O(5)	165.9(2)
Mo−O(2)−C(1)	126.7(3)	Mo−O(3)−C(13)	119.2(3)
Mo−O(4)−C(25)	126.2(3)	Mo−O(5)−C(37)	122.6(3)
C(1)−C(2)−C(14)−C(13)	69.4(7)	C(25)−C(26)−C(38)−C(37)	67.4(7)
MoO(O−Me_2Ph)$_4$ (**8**)			
Mo−O(1)	1.881(2)	Mo−O(2)	1.681(4)
O(1)−Mo−O(2)	104.75(7)	Mo−O(1)−C(1)	146.7(2)

deviated from square-pyramidal to trigonal-bipyramidal: the O1−Mo−O3 bond angle (97.3(2)°) is narrower than O1−Mo−O2 (110.7(2)°), whereas the bond distance of Mo−O3 (1.937(4) Å) is relatively longer (ca. 0.06 Å) than the Mo−O2 distance (1.881(4) Å). Complex **8** is revealed to have a square-pyramidal structure with a crystallographic C_4 axis through Mo and O2. Its coordination geometry is simple and quite similar to that of the corresponding tungsten complex WO(2,6-Me_2-phenolate)$_4$ (**9**).[15d] The Mo═O length (Mo−O2) of **8** is 1.681(4) Å and close to that of complex **1**. The Mo−O1 distance (1.881(2) Å) is also almost equal to Mo−O2 of **1**, which implies that the Mo−O3 bond distance of **1** is elongated, owing to the steric hindrance of the large ring substituents in the biphenolate groups. The bond angle of O1−Mo−O2 (104.75(7)°) is a medium value compared with O1−Mo−O3 and O1−Mo−O2 of complex **1**.

Considering the results of X-ray diffraction studies for **1** and **8**, it can be speculated that all the complexes **1**−**9** should have similar C_2 (or C_4 for **9**) symmetric square-pyramidal structures with the terminal oxo ligand in the apical position.

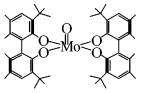
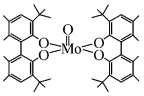
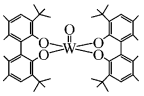
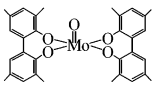
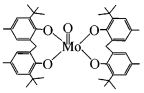
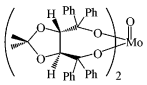
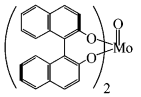
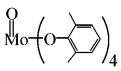
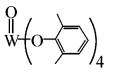
DCPD Polymerization and Subsequent Hydrogenation of the Resulting Poly(DCPD). Table 3 summarizes the results of DCPD polymerization using several Mo and W catalysts and the subsequent hydrogenation of the obtained poly(DCPD)s. Catalyts **1**−**8** were effective for the DCPD polymerization, giving polymers with molecular weights ranging from 3000 to 70 000. However, polymerization with **9** caused slight gelation probably owing to its high molecular weight. As reported previously, our ^{1}H NMR study suggested that all the present poly(DCPD)s were linear and non-cross-linked polymers through selective ROMP of strained norbornene ring.[8d] Further, we have investigated the polymerization of 5,6-dihydro-DCPD by catalysts **1**−**9**, but no vinyl addition-type oligomer was obtained. This result also supports the complete linearity of the present poly(DCPD)s.[8d]

It is interesting that the cis content of the poly(DCPD)s depends on the phenolate ligands in the complexes. Actually, the poly(DCPD)s obtained from **5** and **8** exhibited no cis regularity (cis/trans ∼ 50/50), while the introduction of binaphtholate group (**7**) or taddolate group (**6**) onto MoO(OAr)$_4$ enhanced the cis contents up to 80%. Especially, the use of **1**−**4**, which possess substituted biphenolate groups, gave rise to the cis contents of the polymers up to 90%. The low solubility of these poly(DCPD)s in ordinary solvents at room temperature indicated that these polymers were highly stereoregular. In the ROMP by classic catalyst, main catalyst's ligands, cocatalyst, additives, solvent, polymerization temperature, and even monomer/catalyst ratio often influenced the cis/trans ratio.[3,8] In Table 3, only the main catalyst's ligands were varied, and other parameters were fixed to determine the effect of ligand of cis regularity. It appears very difficult to correlate the cis/trans ratio with the bulkiness/structure of the ligand in the present polymerization system. However, one can say that sterically large ligand tends to lead the polymerization to high cis selectivity.

To know how the structures of the phenolate ligands affected the stereochemistry (i.e., tacticity of the polymer obtained) of the polymerization by ^{13}C NMR, hydrogenation of the poly(DCPD)s was then conducted. The hydrogenated poly(DCPD)s (H-poly(DCPD)s) produced by **4**−**8** were soluble, while those produced by catalysts **1**−**3** were entirely insoluble in ordinary solvents at room temperature and slightly soluble in *o*-dichlorobenzene at high temperature. Therefore, the tacticities of the H-poly(DCPD)s were determined by ^{13}C NMR at high temperature (150 °C), and the recorded NMR charts are illustrated in Figure 3.[16] There was no significant stereoselectivity in the polymerizations using **7** and **8** as main catalysts. In contrast, isotactic bias (m = 60−70%) was observed in ^{13}C NMR spectra of the H-poly(DCPD)s prepared by **4**, **5**, and **6**. It is noteworthy that the H-poly(DCPD)s formed with bulky biphenolate complexes (**1**−**3**) were highly isotactic (meso > 95%).

According to the stated above, it can be concluded that Mo and W biphenolate catalysts (**1**−**3**) induced the stereospecific ROMP (m/r ∼ 95/5) of *endo*-dicyclopentadiene.[9] Before the present investigation, we speculated that binary catalysts would produce atactic poly(DCPD) because the cocatalyst may alkylate a Mo complex at random to produce many kinds of propagating species that may be deprived of ligands. Contrary to our expectation, MoO(*rac*-biphenolate)$_2$−*n*-BuLi induced the stereospecific polymerization successfully. It is interesting that the ligand exchange between Mo and *n*-BuLi appears to proceed smoothly and mildly. We believe it is significant discovery that binary catalysts can control the stereochemistry of the metathesis reaction. The present finding may enlarge the application of binary catalysts to many kinds of precise olefin metathesis reactions.

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

				poly(DCPD)s		hydrogenated poly(DCPD)s[c]	
catalysts		M_n[b]	M_w/M_n[b]	*cis/trans*	T_g, T_m	m/r	T_g, T_m
	***1***	3 700	2.3	85/15	T_m 265 °C 26 J/g	95/5[d]	T_m 292 °C 45 J/g
	***2***	3 700	2.4	85/15	T_m 263 °C 24 J/g	95/5[d]	T_m 292 °C 44 J/g
	***3***	3 900	2.4	91/9	T_m 264 °C 29 J/g	96/4[d]	T_m 292 °C 45 J/g
	***4***	7 700	2.9	88/12	T_g 151 °C	71/29	T_m 257 °C 30 J/g
	***5***	65 000	2.2	47/53	T_g 163 °C	67/33	T_g 101 °C
	***6***	8 700	2.3	84/16	T_g 139 °C	63/37	T_g 100 °C
	***7***	28 000	2.1	67/33	T_g 152 °C	50/50	T_g 106 °C
	***8***	18 700	2.1	40/60	T_g 150 °C	56/44	T_g 105 °C
	***9***	gelation		—	T_g 130 °C	—	—

[a] Polymerized in cyclohexane at 80 °C for 2 h; $[DCPD]_0 = 1.3$ M, [1-octene] = 26 mM, [Mo or W complex] = 1.3 mM, [Mo or W complex]: [*n*-BuLi] = 1:2, all the polymer yields are 100%. [b] Before hydrogenation. [c] The extent of hydrogenation was >99%. Olefinic signals were no longer present in the ^{1}H NMR spectra of all the H-poly(DCPD)s. Hydrogenated in cyclohexane at 160 °C for 8 h; $[Ru(Cy_3P)_2Cl_2(=CHOEt)]$/[DCPD unit] = 1/1000 in mole ratio, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa. [d] Hydrogenated in cyclohexane at 160 °C for 8 h; $[Ni(OAc)_2]$/[DCPD unit] = 1/100 in mole ratio, $[Ni(OAc)_2]$:[*i*-Bu_3Al] = 1:4, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa.

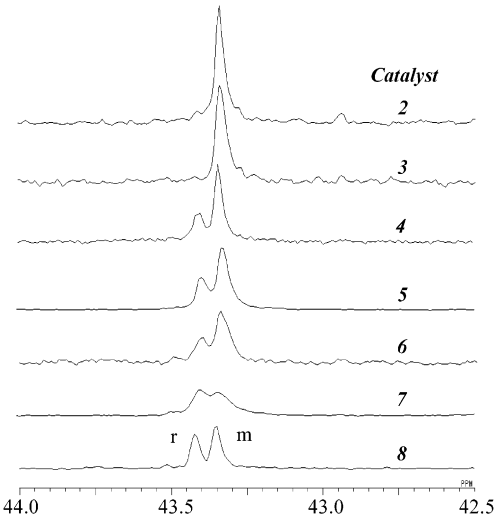


Figure 3. ^{13}C NMR spectra of methine carbon in the main chain of H-poly(DCPD) shown in Table 3.

The isotacticity in poly(DCPD) by **1**−**3** is supposed to arise from the enantiomorphic site control.[7] That is, the bulkier "biphen" ligand, which is designed by Schrock and Hoveyda for their catalyst,[7j] remains on the present propagating species and controls the coordination of DCPD effectively. Catalyst **4**, which has less bulky 3,3′,5,5′-Me_4-biphenolate ligands, is expected to regulate the polymerization in the same fashion. However, its isospecificity was rather low (m/r = 71/29) and did not meet our expectation. It is plausible that Me groups in 3 and 3′ positions are not bulky enough to influence the coordination of DCPD. On the contrary, nonsubstituted binaphtholate **7** has no ability to control the tacticity (m/r = 50/50). In the case of catalysts **1**−**4** and **7**, which possess biphenolate as ligand, the isospecificity of the polymerization appears to increase with increasing the size of the substituents in the ortho position of biphenolate. Taddolate complex **6** exhibited low stereoselectivety as compared to "biphen" complexes **1**−**3**. Such a tendency regarding the stereospecificity of polymerization with the present system is similar to those with Schrock catalyst's systems.[7b] As ^{1}H NMR spectra of **5** suggested that it has the C_{2v} symmetric structure, we have supposed that **5** would produce atactic poly(DCPD). In contradiction to our expectation, catalyst **5** promoted the iso-biased polymerization (m/r = 67/33). At this stage we have no information about the propagating species structure of **5**, however speculating perhaps the *t*-Bu groups on the bisphenolate may have steric hindrance effect on the coordination of DCPD. Catalyst **8** polymerized DCPD to yield an atactic polymer suggests that the polymerization process is not

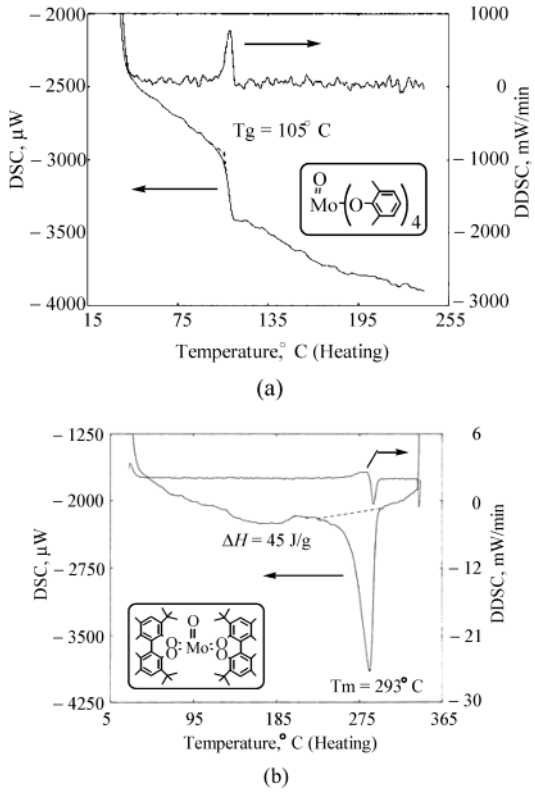


Figure 4. DSC thermograms of H-poly(DCPD)s obtained by **8**-based (a) and **2**-based (b) catalysts in Table 3 (determined on the first heating scan under N_2 for 10 °C /min).

regulated by chain end or enantiomorphic metal site control.

Properties of the Poly(DCPD)s and the Hydrogenated Poly(DCPD)s. The poly(DCPD)s were characterized by DSC. As shown in Table 3, the poly(DCPD)s obtained with **4**−**9** exhibited glass transition point at 130−160 °C, while **1**−**3** provided insoluble poly(DCPD)s with melting point at 260 °C. The thermal properties of the H-poly(DCPD)s were also investigated, and the DSC charts of the polymers obtained with **2** and **8** are shown in Figure 4. The atactic H-poly(DCPD)s from **5**−**8** exhibited glass transition point at 100−105 °C (e.g., Figure 4a for **8**), as observed for the polymers formed with classic ROMP catalysts such as WCl_6-based systems.[8e,f,9] This suggests that these polymers are amorphous. In sharp contrast, the highly isotactic H-poly(DCPD)s, which were yielded by the bulkier biphenolate complexes **1**−**3**, displayed a large endothermic peak at an elevated temperature and no glass transition (Figure 4b for **2**). Furthermore, the crystallinities of these nonannealed isotactic H-poly(DCPD)s were estimated to be about 57% by XRD.[18] These results clearly indicate that these isotactic H-poly(DCPD)s are highly crystalline polymers. Methyl-substituted biphenolate **4** yielded crystalline polymer whose isotacticity was only 70%, while the slightly less isotactic-biased H-poly(DCPD)s (m = 60−70% produced by **5** and **6**) showed amorphousness. The relationship between stereoregularity and higher-order structure (amorphous or crystalline) in the H-poly(DCPD)s is not yet clearly understood. The information about the triad structure might hold the key, and our investigation is now in progress to determine the relationship.

In conclusion, the bulkier biphenolate complexes **1**−**3** proved to be effective for the production of higher crystalline hydrogenated poly(DCPD). It is interesting that the thermal property of H-poly(DCPD) obtained with MoO(*rac*-biphenolate)$_2$ (**2**) was essentially the same with that obtained with MoO((*R*)-(+)-biphenolate)$_2$ (**1**). This stimulated further investigation of catalyst **2** with the NBE polymerization.

Development of Highly Crystalline Hydrogenated Poly(NBE). We have studied the polymerization of NBE with the motivation to know how MoO(*rac*-biphenolate)$_2$ (**2**) influences the stereoselectivity of NBE polymerization. We have also employed MoO(O-Me_2Ph)$_4$ (**8**) to make a comparison with MoO(*rac*-biphenolate)$_2$ (**2**). NBE polymerization was carried out under the following conditions: in cyclohexane at 80 °C for 2 h; $[NBE]_0$ = 1.8 M, [1-octene] = 36 mM, [Mo complex] = 1.8 mM, [Mo complex]:[*n*-BuLi] = 1:2. Hydrogenation of poly(NBE)s was conducted in the following conditions: in cyclohexane at 160 °C for 8 h; [$Ru(Cy_3P)_2Cl_2$(=CHOEt)]/[NBE unit] = 1/1000 in mole ratio, [poly(NBE)] = 5 wt %, H_2 = 1.0 MPa.

In the presence of MoO(*rac*-biphenolate)$_2$−*n*-BuLi, polymerization of NBE proceeded rapidly and ended up with the formation of soluble poly(NBE) (polymer yield = 100%, M_n = 26 000, M_w/M_n = 3.9, cis content > 99.5%). The subsequent hydrogenation of the poly(NBE) provided an insoluble hydrogenated poly(NBE) (H-poly(NBE)), of which extent of hydrogenation is ∼100%. It was difficult to evaluate the m/r ratio of H-poly(NBE), since the polymer was almost insoluble to $CDCl_3$ at 60 °C. However, the low solubility of H-poly(NBE)/**2** may indicate its tactic structure. MoO(O−Me_2Ph)$_4$ (**8**) also provided soluble poly(NBE) quantitatively (polymer yield ∼100%, M_n = 83 300, M_w/M_n = 2.2, cis/trans = 30/70). The successive hydrogenation was carried out to produce a soluble H-poly(NBE), of which hydrogenation ratio is ∼100%. The tacticity of the H-poly(NBE)/**8** was determined to be about m/r = 45/55, owing to the polymer's high solubility to $CDCl_3$.[19]

The thermal property of these H-poly(NBE)s was characterized by DSC. An atactic H-poly(NBE) provided by **8** showed an endothermic peak at low temperature (T_m = 136 °C, ΔH = 46 J/g) (Figure 5a). This indicates that the H-poly(NBE) is essentially crystalline polymer even though its backbone is atactic. The H-poly(NBE) obtained from **2** had a higher melting point with a larger melting enthalpy (T_m ∼ 172 °C, ΔH = 60 J/g) (Figure 5b). The XRD pattern of H-poly(NBE)/***2*** showed many crystalline reflections, supporting its high crystallinity.[19]

These results indicate that the present "tactic" H-poly(NBE)/**2** was a highly crystalline polymer. We believe a novel method was developed to produce highly crystalline H-poly(NBE) using the MoO(*rac*-biphenolate)$_2$−*n*-BuLi catalyst system. It is also interesting that there are two endothermic peaks in DSC (i.e., the first peak at 150 °C and the second one at 172 °C) in the tactic H-poly(NBE). This fact suggests that tactic H-poly(NBE) may form more than one kind of different crystal structure.[20]

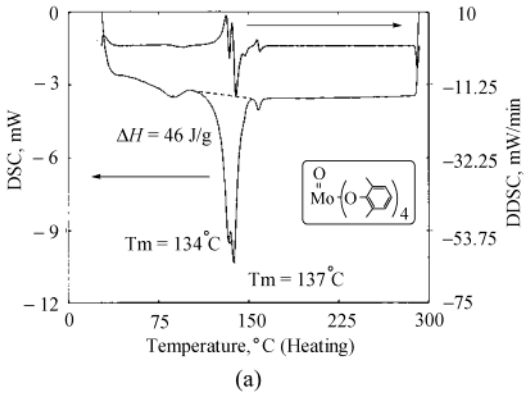
Effects of Reaction Conditions. Effects of reaction conditions on the polymerization of DCPD by catalyst type **2** were investigated in more detail. The polymerization was carried out under the following conditions unless otherwise noted: in cyclohexane at 80 °C for 2 h; $[DCPD]_0$ = 1.3 M, [1-octene] = 26 mM, [Mo or W complex] = 1.3 mM.

The effect of the cocatalysts was examined in the polymerization of DCPD by MoO(*rac*-biphenolate)$_2$−

Table 4. Effects of Cocatalysts for the Polymerization of DCPDby MoO(*rac*-biphenolate)$_2$−Cocatalyst Systems[a]

					T_m and ΔH	
cocatalysts	[Mo]:[cocat]	polymer yield	M_n[b]	M_w/M_n[b]	poly(DCPD)s	hydrogenated poly(DCPD)s[c]
none	1:0	no polymer				
n-BuLi	1:1	83%	5700	2.0	270 °C, 19 J/g	294 °C, 39 J/g
n-BuLi	1:2	100%	4400	2.1	264 °C, 21 J/g	293 °C, 38 J/g
n-BuLi	1:3	no polymer				
Et_3Al	1:1	50%	10500	2.7	267 °C, 8 J/g	286 °C, 39 J/g
n-Bu_4Sn	1:1	no polymer				
MeMgI	1:2	gelation				

[a] Polymerized in cyclohexane at 80 °C for 2 h; $[DCPD]_0 = 1.3$ M, [1-octene] = 26 mM, [Mo or W complex] = 1.3 mM. [b] Before hydrogenation. [c] Hydrogenated in cyclohexane at 160 °C for 8 h; $[Ni(OAc)_2]$/[DCPD unit] = 1/100 in mole ratio, $[Ni(OAc)_2]$:[*i*-Bu_3Al] = 1:4, [poly(DCPD)] = 5 wt %, H_2 = 1.0 MPa.



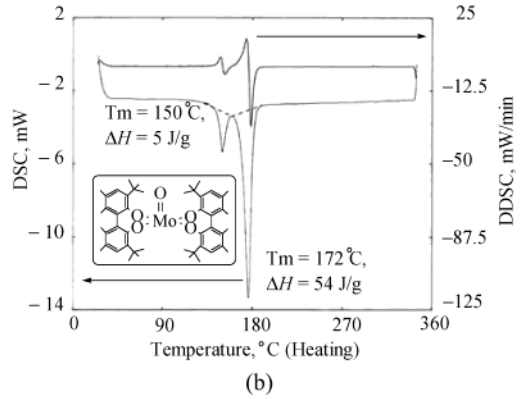


Figure 5. DSC thermograms of H-poly(NBE) produced by **8** (a) and **2** (b) (polymerized in cyclohexane at 80 °C for 2 h; $[NBE]_0 = 1.8$ M, [1-octene] = 36 mM, [Mo complex] = 1.8 mM, hydrogenated in cyclohexane at 160 °C for 8 h; $[Ru(Cy_3P)_2Cl_2(=CHOEt)]$/[NBE unit] = 1/1000 in mole ratio, [poly(NBE)] = 5 wt %, H_2 = 1.0 MPa; determined on the second heating scan under N_2 for 10 °C /min).

cocatalyst (1:*x*) (Table 4). MoO(*rac*-biphenolate)$_2$ (**2**) does not have polymerization activity in the absence of a cocatalyst. When *n*-BuLi was added to MoO(*rac*-biphenolate)$_2$, polymerization was induced, resulting in insoluble poly(DCPD)s with high crystallinity. On the other hand, when *n*-BuLi was employed in 3-fold excess, no polymer was obtained. Et_3Al was also useful as a cocatalyst of MoO(*rac*-biphenolate)$_2$, whereas its activity was considerably lower in comparison with that of *n*-BuLi. No poly(DCPD) was obtained by using MoO(*rac*-biphenolate)$_2$−*n*-Bu_4Sn (1:1). The transalkylation between MoO(*rac*-biphenolate)$_2$ and *n*-Bu_4Sn (i.e., catalyst activation) probably did not occur due to the low basicity of *n*-Bu_4Sn. The polymerization in the presence of MoO(*rac*-biphenolate)$_2$−EtMgI ended in the gelation to yield an amorphous polymer. The *n*-BuLi and Et_3Al turned out to be effective cocatalysts to promote stereospecific ROMP, and 2-fold of *n*-BuLi seems to be more

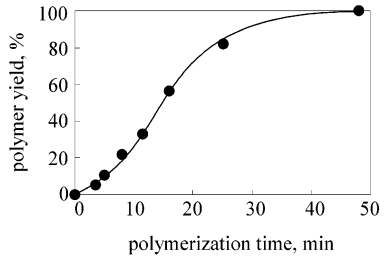


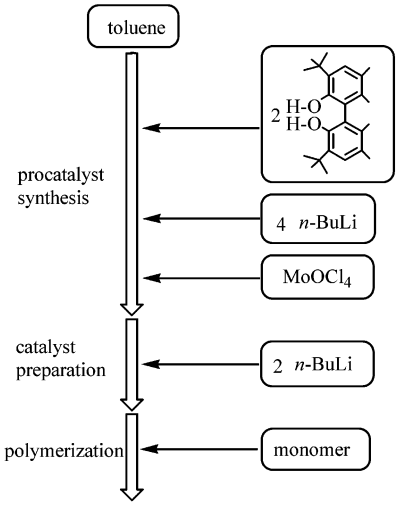
Figure 6. Time profile of the polymerization of DCPD with MoO(*rac*-biphenolate)$_2$−*n*-BuLi (1:2) (polymerized in cyclohexane at 80 °C; $[DCPD]_0 = 1.3$ M, [1-octene] = 26 mM, [MoO(*rac*-biphenolate)$_2$] = 1.3 mM).

favored. Unfortunately, no information about the propagating species has been obtained in the present M(=O)(O−Ar)$_x$−*n*-BuLi binary ROMP system. However, the initiation mechanism and the structure of the initiating species can be speculated as follows: Reaction of MoO(*rac*-biphenolate)$_2$ (**2**) with 2-fold *n*-BuLi generated a dialkyl species (*n*-$C_4H_9)_2$Mo(=O)(*rac*-biphenolate). Then the *n*-butyl group on the Mo becomes an *n*-butylidene by α-H elimination, based on the information obtained from the literature.[17] Taking into account the report about the stereospecific polymerizations by the Schrock−Hoveyda catalyst,[7a−e,9] it is plausible that the above-stated molybdenum *n*-butylidene [*n*-C_3H_7CH=Mo(=O)(*rac*-biphenolate)] induces the present stereospecific polymerization.

The effects of reaction time and temperature were examined. A time profile of the polymerization of DCPD was studied by using MoO(*rac*-biphenolate)$_2$−*n*-BuLi (1:2) at 80 °C. The time−polymer yield curve is depicted in Figure 6. In the early stage of the reaction, one can see that the polymerization is rather slow. This indicates that the initiation reaction is much slower than the propagation reaction. Polymerization proceeded at moderate rate and finished within 50 min at the 80 °C reaction temperature. The polymerization temperature was changed to determine the effect of the reaction rate. At 0 °C, polymerization became very slow; the polymer yield was 2% after 2 h reaction. The results of the polymerization at other temperatures were as follows: at 20 °C, polymer yield 22% for 2 h and 77% for 24 h; at 50 °C, polymer yield 90% for 2 h. From the stated above, polymerization with Mo or W complexes−*n*-BuLi (1:2) was conducted at 80 °C for 2 h in the following investigation on the effect of the monomer/catalyst ratio.

The catalyst activity was investigated in the polymerization of DCPD. When DCPD in 1000-fold excess was employed for the polymerization, catalyst systems **1**−**9** consumed monomer completely within 2 h at 80 °C. When 2500 equiv of DCPD was used, the polymerizations were saturated at 30−80% in the case of catalyst

Scheme 6. One-Pot Catalyst Preparation



systems **4**−**9**, whereas the polymer yields reached 90% and 100% with the bulkier biphenolate complexes **2** and **3**, respectively. Particularly, the tungsten catalyst **3** can be characteristic in extremely high activity: the polymer yield was 100% when the monomer/catalyst ratio was the 10 000/1, and the polymer yield was 95% even when the monomer/catalyst was 20 000/1 (polymerized in cyclohexane at 80 °C for 2 h). It can be emphasized that the catalyst activity of **3** is higher than the Schrock−Hoveyda catalyst. As reported, the Schrock−Hoveyda catalyst polymerized 5000-fold of DCPD quantitatively.[9] The polymerization was investigated to gain information about the Schrock−Hoveyda activity. There was no polymer produced with a DCPD/catalyst ratio 10 000/1 (polymerized in cyclohexane at 50 °C for 3 h; $[DCPD]_0$ = 1.3 M, [1-hexene] = 13 mM, [Schrock−Hoveyda catalyst] = 0.13 mM).

The possibility of a one-pot catalyst preparation was investigated. In other words, this investigation can be assumed as a study of novel ternary and quarternary catalysts such as $MoOCl_4$−*rac*-biphenolate−*n*-BuLi (1:2:2) and *rac*-biphenol−*n*-BuLi−$MoOCl_4$−*n*-BuLi (2:4:1:2), respectively.

The preparation of the novel quarternary catalyst is described in Scheme 6 as follows: 2 equiv of the *rac*-biphenol and 4 equiv of *n*-BuLi were mixed in toluene at −78 °C and aged at room temperature for 30 min to form Li_2(*rac*-biphenolate). The toluene solution was added to the toluene slurry of $MoOCl_4$ at −78 °C. This mixture was allowed to age at an ambient temperature for 30 min to yield MoO(*rac*-biphenolate)$_2$ (**2**) and 4-fold of LiCl. A dark-blue mixture was formed, and 2 equiv of *n*-BuLi at −78 °C was added. The reaction mixture was aged at room temperature for an additional 15 min and became reddish-orange solution. The color of this solution is very similar to that of the above-stated normal MoO(*rac*-biphenolate)$_2$−*n*-BuLi (1:2) catalyst solution prepared from the isolated **2**. In the presence of this catalyst solution, polymerization of DCPD proceeded smoothly and resulted in the formation of insoluble crystalline poly(DCPD). Its hydrogenated product also showed high melting point (T_m = 288 °C, ΔH = 40 J/g).

Catalyst preparation of the ternary catalyst, $MoOCl_4$−*rac*-biphenolate−*n*-BuLi (1:2:2), was essentially in the same manner as described for the quarternary catalyst: The toluene solution of *rac*-biphen−Li_2 was added to the toluene slurry of $MoOCl_4$ at −78 °C. This mixture was aged at ambient temperature for 30 min. A dark-blue mixture was formed, and 2 equiv of *n*-BuLi at −78 °C was added. The reaction mixture was aged at room temperature for an additional 15 min to eventually become a reddish-orange solution. The present ternary catalyst solution induced the stereospecific polymerization of DCPD successfully.

Therefore, great emphasis can be placed upon the fact that a one-pot catalyst preparation is the effective method to provide crystalline H-poly(DCPD). Namely, we have developed the novel convenient methodology to control the stereoselectivity of the ROMP by use of the novel ternary catalyst [$MoOCl_4$−*rac*-biphenolate−*n*-BuLi (1:2:2)] and the novel quarternary catalyst [*rac*-biphenol−*n*-BuLi−$MoOCl_4$−*n*-BuLi (2:4:1:2)]. We believe this novel convenient methodology may expand the utility of stereospecific ROMP and related metathesis reaction.

Summary

The present study is summarized as follows: Various novel Mo and W complexes of the formula M(=O)(O−Ar)$_4$ (M = Mo or W; (O−Ar)$_4$ is two biphenolate or four phenolate ligands) were synthesized. Mo and W catalysts bearing bulkier biphenolate ligands (**1**−**3**) promoted cis and isospecific ROMP of DCPD (cis ∼ 90% and meso > 90%). The H-poly(DCPD)s, whose meso-diad contents are up to 90%, exhibited melting points at high temperatures (T_m = 292 °C, ΔH = 45 J/g). The H-poly(NBE) yielded by catalyst **2** was also a highly crystalline polymer featuring a high melting point (T_m = 175 °C, ΔH = 60 J/g). We have developed a novel class of crystalline polymer plastics with unique technical properties for future engineering applications.

Acknowledgment. The authors thank Mr. Hirokazu Matsumoto for his helpful discussion and XRD study.

Supporting Information Available: Experimental details, fully labeled ORTEP drawings, final positional parameters, final thermal parameters, bond distances and angles for **1** and **8**; XRD charts of H-poly(DCPD) obtained from **2** (Figure S1), H-poly(DCPD) obtained from **8** (Figure S2), H-poly(NBE) with **2** (Figure S3); and ^{13}C NMR charts of H-poly(NBE) with **2** and H-poly(NBE) with **8** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Yasuda, H. *Prog. Polym. Sci.* **2000**, *25*, 573.
(2) (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465. (b) Ewan, J. A.; Jones, R. J.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
(3) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.
(4) (a) Gilliom, L. R.; Grubbs, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 533. (b) Mashima, K.; Nakayama, Y.; Kaidzu, M.; Ikushima, N.; Nakamura, A. *J. Organomet. Chem.* **1998**, *557*, 3. (c) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules* **2002**, *35*, 1583. (d) Wallace, L. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (e) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127. (f) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.
(5) For a review: (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Hoveyda, A. H.; Schrock, R. R. *Chem.−Eur. J.* **2001**, *7*, 945. (c) Schrock, R. R. *Tetrahedron* **1999**, *55*, 8141. (d) Schrock, R. R. In *Topics in Organometallic Chemistry: Alkene Metathesis in Organic Synthesis*; Fuerstner, A., Ed.; Springer: Berlin, 1998; Vol. 1, p 1.

(6) (a) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (c) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (e) For a review: Fuerstner, A. In *Topics in Organometallic Chemistry: Alkene Metathesis in Organic Synthesis*; Fuerstner, A., Ed.; Springer: Berlin, 1998; Vol. 1, p 37.

(7) (a) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378. (b) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (c) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414. (d) Schrock, R. R.; Lee, J.-K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933. (e) Totland, K. M.; Boyd, J. T.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114. (f) Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652. (g) Tsang, W. C. P.; Jernelius, J. A.; Cortez, G. A.; Weatherhead, G. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2591. (h) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2001**, *40* 1452. (i) Alexander, J. B.; Schrock, R. R.; Davis, W. M.; Hultzsch, K. C.; Hoveyda, A. H.; Houser, J. H. *Organometallics* **2000**, *19*, 3700. (j) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041.

(8) (a) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1986**, *36*, 115. (b) Al-Samak, B.; Ebrahimi, V. A.; Carvill, A. G.; Hamilton, J. G.; Rooney, J. J. *Polym. Int.* **1996**, *41*, 85. (c) Carvill, A. G.; Greene, R. M. E.; Hamilton, J. G.; Ivin, K. J.; Kenwright, A. M.; Rooney, J. J. *Macromol. Chem. Phys.* **1998**, *199*, 687. (d) Davidson, T. A.; Wagener, K. B.; Priddy, D. B. *Macromolecules* **1996**, *29*, 786. (e) Kodemura, J.; Natsuume, T. *Polym. J.* **1995**, *27*, 1167. (f) Kohara, T. *Macromol. Symp.* **1996**, *101*, 571.

(9) (a) Hayano, S.; Kurakata, H.; Uchida, D.; Sakamoto, M.; Kishi, N.; Matsumoto, H.; Tsunogae, Y.; Igarashi, I. *Chem. Lett.* **2003**, 670. (b) Hayano, S.; Kurakata, H.; Tsunogae, Y. Japanese Laid-Open Patent Publication No. 2002-249553.

(10) Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 579.

(11) (a) Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Inorg. Chem.* **2000**, *39*, 5412. (b) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153.

(12) (a) Higashi, T. Program for Absorption Correction, Rigaku Corp., Tokyo, Japan, 1999. (b) Larson, A. C. 1970, Crystallographic Computing, 291-294. Ahmed, F. R., Ed., Munksgaard, Copenhagen (eq 22, with *V* replaced by the cell volume).

(13) (a) Sheldrick, G. M. Program for the Solution of Crystal Structure. University of Goettingen, Germany. (b) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(14) (a) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994. (b) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

(15) (a) Nakayama, Y.; Mashima, K.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1496. (b) Kolodziej, R. M.; Schrock, R. R.; Dewan, J. C. *Inorg. Chem.* **1989**, *28*, 1243. (c) Diez, S. D.; Eilerts, N. W.; Heppert, J. A.; Morton, M. D. *Inorg. Chem.* **1993**, *32*, 1698. (d) Bell, A. *J. Mol. Catal.* **1992**, *76*, 165. (e) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *J. Organomet. Chem.* **1985**, *296*, 55. (f) Bell, A. US Patent 5,194,-534, 1993. (g) Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483. (h) Kanehisa, N.; Kai, Y.; Kasai, N.; Yasuda, H.; Nakayama, Y.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1197. (i) Lehtonen, A.; Sillanpaeae, R. *Polyhedron* **2002**, *21*, 1017. (j) Lehtonen, A.; Sillanpaeae, R. *Inorg. Chem. Commun.* **2001**, *4*, 108. (k) Griffith, W. P.; Nogueira, H. I. S.; White, A. J. P.; Williams, D. J. *Polyhedron* **1997**, *16*, 1323.

(16) Thus far, the microstructure of H-poly(DCPD) had been studied in detail.[8c] Signal splittings owing to tacticity had been observed in polymer; however, its assignment of signals to m and r dyads had not been accomplished in the ^{13}C NMR spectra. According to the combination of our NOESY study and MOPAC simulation of polymer backbone, the signal at 43.35 ppm may be assigned to m dyad, and 44.25 ppm is to r dyad. Therefore, we suppose the present catalyst systems promote isospecific polymerization.

(17) (a) Ivin, K. J.; Milligan, B. D. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 269. (b) Hayano, S.; Masuda, T.; Ji, H.; Advincula, R. C. *Polym. Bull. (Berlin)* **2000**, *44*, 129. (c) Nakayama, Y.; Saito, H.; Ueyama, N.; Nakamura, A. *Organometallics* **1999**, *18*, 3149. (d) Nakayama, Y.; Ikushima, N.; Ueyama, N.; Nakamura, A.; Harada, A. *Chem. Lett.* **2000**, 434.

(18) The crystallinity of crystalline H-poly(DCPD) was estimated by XRD as follows: At first, amorphous halo was determined using a complete amorphous H-poly(DCPD) prepared from **8**. Then, the XRD pattern of crystalline H-poly(DCPD) was recorded. Reflections owing to the crystalline region were separated from halo of amorphous region, and the crystallinity was calculated using the crystalline/amorphous area ratio. XRD patterns of crystalline H-poly(DCPD)s obtained from **1**−**3** are essentially identical, and crystallinities of them were almost the same value. XRD charts of H-poly(DCPD) obtained from **2** (Figure S1) and H-poly(DCPD) obtained from **8** (Figure S2) are available in the Supporting Information.

(19) The XRD chart of H-poly(NBE) with **2** (Figure S3) is available in the Supporting Information. ^{13}C NMR charts of H-poly-(NBE) with **2** and H-poly(NBE) with **8** (Figure S4) are also available in the Supporting Information.

(20) Before the annealing, ΔH of the first peak is larger than that of second one in the DSC measurement (first peak: T_m = 152 °C, ΔH = 15 J/g; second peak: T_m = 168 °C, ΔH = 45 J/g), and total ΔH was about 60 J/g. The annealing diminished the melting enthalpy of the first peak (T_m = 150 °C, ΔH = 5 J/g) and enlarged that of second one (T_m = 172 °C, ΔH = 54 J/g), whereas the total ΔH was maintained about 60 J/g. Moreover, the XRD pattern of the annealed polymer was largely different from that of nonannealed one. We suppose that crystalline H-poly(NBE) can form many kind of different crystal structure, and the ratio of them depends on the crystallization condition.

MA034611Y