# Syndiospecific Ring-opening Metathesis Polymerization of *endo*-Dicyclopentadiene by Tungsten(VI) Phenylimido Catalyst

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cis- and syndio-Specific ring-opening metathesis polymerization of *endo*-dicyclopentadiene was achieved for the first time by the newly developed catalyst, $W(=N\text{-}Ph)Cl_4 \cdot Et_2O$–$Et_2Al(OEt)$, to produce crystalline syndiotactic hydrogenated poly(*endo*-dicyclopentadiene).

In general, organometallic catalysts are recognized as an effective means to realize the precise polymerizations. The precise ring-opening metathesis polymerization (ROMP) of cycloolefins has also been under intensive research.[1] It is well known that the development of metal carbene complexes has enabled the living and/or stereospecific ROMP of several cycloolefins. The Schrock catalysts, molybdenum alkylidene complexes, have made significant progress with precise ROMP.[2] An extensive number of excellent ruthenium carbenes (Grubbs' catalysts) have made a great influence upon the metathesis chemistry including ROMP of cycloolefins.[3]

The stereospecific ROMP has been studied well in the past decades. In the case of ring-opened poly(norbornene), there are two steric structural factors (cis/trans and meso/racemo) in the polymer main chain. The isospecific ROMP of cycloolefins was investigated by using Schrock catalysts and Schrock–Hoveyda catalysts in great deal.[2,4] Recently, we have reported that the molybdenum diolate catalyst induced the cis- and isospecific ROMP of *endo*-dicyclopentadiene (DCPD), and the following hydrogenation produced the isotactic hydrogenated poly(DCPD) (H-poly(DCPD)), which was characteristic in high melting point (for the first scan: $T_m = 290\,°C$, $\Delta H = 40\,J/g$).[5] Isospecificity of these ROMP systems is supposed to originate from the enantiomorphic site control caused by the bulky diolate ligand.[2,5] On the other hand, the syndiospecific ROMP of aliphatic cycloolefins is supposed to have been partially unachieved. There are few studies on the syndiospecific ROMP of norbornenes.[6]

In this paper, we have focused our attention on the development of the new and versatile W-imido catalysts effective for the syndiospecific ROMP of DCPD (Scheme 1). This article also reports the effects of the ligand structures on the syndioselectivity of the polymerization, and the development of syndiotactic H-poly(DCPD) as a new crystalline polymer plastics (Scheme 2).

Tungsten(VI) imido tetrachloride complexes ($W(=N\text{-}R)Cl_4 \cdot Et_2O$) were selected as main catalysts. $WCl_6$ was chosen as a starting material. $WOCl_4$ was synthesized from $WCl_6$ and hexamethyldisiloxane in methylene chloride.[7] Then $WOCl_4$ as catalyst precursor was treated with an equimolar of isocyanate in toluene under reflux condition, and the crude insoluble product of $(W(=N\text{-}R)Cl_4)_n$ was obtained in a high yield.[8] This product could be recrystallized from suitable solvents such as diethyl ether/*n*-hexane to yield highly pure products of $W(=N\text{-}R)Cl_4 \cdot Et_2O$. The following complexes were successfully prepared: $W(=N\text{-}Ph)Cl_4 \cdot Et_2O$ (**1**), $W(=N\text{-}2,6\text{-}Me_2\text{-}Ph)Cl_4 \cdot Et_2O$ (**2**), and $W(=N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}Ph)Cl_4 \cdot Et_2O$ (**3**).[9]

Table 1 summarizes the results of the optimized DCPD polymerization using several W-imido catalysts and the subsequent hydrogenation of the obtained poly(DCPD)s, including the characterization of the microstructures of the poly(DCPD)s and H-poly(DCPD)s.[10] In the DCPD polymerization, three equivalents of $Et_2Al(OEt)$ was employed as cocatalyst to activate the W-imido catalysts, and an adequate amount of 1-octene was added as a chain-transfer agent to control the molecular weight of the resulting poly(DCPD)s in the moderate range. W-imido binary catalysts displayed notable ROMP activity for DCPD to afford poly(DCPD)s in quantitative yields. The $^1H$ NMR study suggested that the present poly(DCPD)s were linear and non-crosslinked polymers through selective ROMP of the strained norbornene ring. It is interesting that the cis-content of the poly(DCPD)s depends on the structure of the tungsten imido catalysts. $W(=N\text{-}Ph)Cl_4 \cdot Et_2O$ induced highly cis-regular polymerization. While the introduction of substituents on the 2,6-position of the phenyl ring obviously led to a decrease in the cis-ratio of the polymers provided.

With the motivation to know how the structures of the imido ligands affected the stereochemistry of the polymerization, hydrogenation of the poly(DCPD)s was conducted next. The selected NMR charts of H-poly(DCPD)s obtained from W-imido systems were illustrated in Figure 1. It is noteworthy that the phenylimido catalyst **1** promoted cis- and syndio-specific ROMP of DCPD. On the contrary, the H-poly(DCPD) obtained from **2** was a less tactic polymer. Further, the introduction of isopropyl groups on the 2,6-position of the phenyl ring obviously gave rise 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. However, it remained unknown
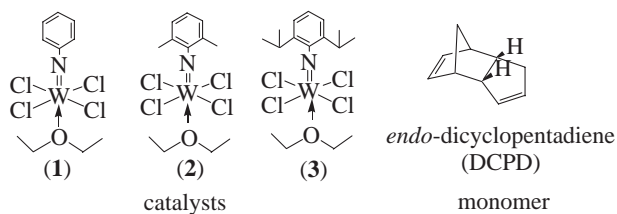


**Scheme 1.** Catalysts and monomer in this study.
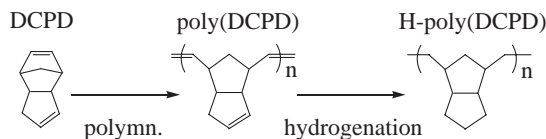


**Scheme 2.** Production of hydrogenated poly(DCPD).

**Table 1.** Polymerization of DCPD by tungsten imido 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] | | |
| | | | cis/trans | Thermal properties | m/r | Thermal properties | |
| | | | | | | 1st scan | Annealed |
|---|---|---|---|---|---|---|---|
| **1** | 10 000 | 3.5 | 93/7 | $T_g$, 151 °C | 20/80 | $T_m$, 272 °C $\Delta H = 52$ J/g | $T_m$, 258 °C $\Delta H = 39$ J/g |
| **2** | 27 000 | 6.0 | 86/14 | $T_g$, 149 °C | 33/67 | $T_m$, 240 °C $\Delta H = 37$ J/g | $T_m$, 234 °C $\Delta H = 4$ J/g |
| **3** | 16 000 | 3.1 | 72/28 | $T_g$, 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 M = 1 mol dm$^{-3}$), [1-octene] = 50 mM, [W-imido] = 1.3 mM, [Et$_2$Al(OEt)] = 3.6 mM, all polymer yields are 100%. [b]Before hydrogenation. [c]Hydrogenated in cyclohexane at 160 °C for 16 h; [Ru(Cy$_3$P)$_2$Cl$_2$(=CHOEt)]/[DCPD unit] = 1/1000 in mol ratio, [poly(DCPD)] = 5 wt %, H$_2$ = 1.0 MPa, all hydrogenation ratios are 100%.
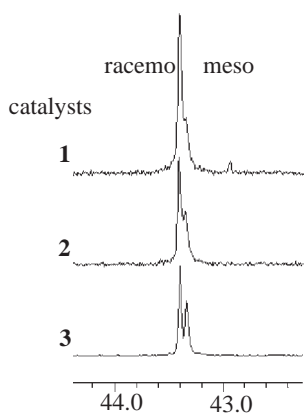


**Figure 1.** Selected $^{13}$C NMR spectra of methine carbon in the main chain of H-poly(DCPD)s shown in Table 1.

how the imido ligands control the polymerization process. At least it is assumable that the syndiotacticity in poly(DCPD) by the present catalysts is supposed to arise from the chain-end tacticity control, and the bulky substituents might have canceled the stereoregulation effects from the chain-end.[2]

Afterwards, H-poly(DCPD)s were characterized by DSC. It is worth noting that the syndiotactic H-poly(DCPD), which was yielded by **1**, displayed a large endothermic peak at an elevated temperature on the first scan. Rapid crystallization was also observed in the cooling trace ($T_c = 197$ °C, $\Delta H = 38$ J/g). Further, the annealed syndiotactic H-poly(DCPD) also possessed high melting point and large melting enthalpy. These results clearly indicate that the syndiotactic H-poly(DCPD) is a crystal-line polymer. The slightly tactic H-poly(DCPD), which was produced by **2**, exhibited very small crystal fusing. The atactic H-poly(DCPD) obtained from **3** showed only glass transition point at 100 °C, as observed for the polymers formed with classic catalysts.[5]

To conclude the present article, we have reported for the first time that the W(=N-Ph)Cl$_4$·Et$_2$O-based catalyst induced the syndiospecific ROMP of DCPD to develop a crystalline syndio-tactic H-poly(DCPD), which could be regarded as a new crystal-line polymer plastic for future engineering applications. The detail investigations of the polymerization and of the properties of the syndiotactic H-poly(DCPD) are now in progress.

**References and Notes**

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9   **1**: $^1$H NMR (C$_6$D$_6$) δ 6.97–6.87 (m, 4H, H$_{aryl}$), 6.16 (t, 1H, H$_{aryl}$), 4.43 (q, 4H, Et$_2$O), 1.08 (t, 6H, Et$_2$O); $^{13}$C NMR (C$_6$D$_6$) δ 149.8, 134.0, 131.4, 127.2, 66.3, 13.1. Anal. Calcd for C$_{10}$H$_{15}$Cl$_4$NOW: C, 24.47; H, 3.08; N, 2.85%. Found, C, 24.24; H, 3.00; N, 2.90%. **2**: $^1$H NMR (C$_6$D$_6$) δ 6.73 (d, 2H, H$_{aryl}$), 5.88 (t, 1H, H$_{aryl}$), 4.07 (brs, 4H, Et$_2$O), 3.30 (s, 6H, CH$_3$), 1.08 (t, 6H, Et$_2$O); $^{13}$C NMR (C$_6$D$_6$) δ 148.3, 145.5, 133.8, 126.1, 65.9, 17.7, 13.8. Anal. Calcd for C$_{12}$H$_{19}$Cl$_4$NOW: C, 27.77; H, 3.69; N, 2.70%. Found: C, 27.94; H, 3.76; N, 2.80%. **3**: $^1$H NMR (C$_6$D$_6$) 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$_2$O), 1.34 (d, 12H, CH$_3$), 1.06 (t, 4H, Et$_2$O); $^{13}$C NMR (C$_6$D$_6$) 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$_4$NOW: C, 33.42; H, 4.73; N, 2.44%. Found: C, 34.35; H, 4.82; N, 2.53%.

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