Stereospecific Ring-Opening Metathesis Polymerization of *endo*-Dicyclopentadiene by Schrock–Hoveyda Catalyst and Novel Mo- and W-based Complexes. Development of Crystalline Hydrogenated Poly(*endo*-dicyclopentadiene)

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Novel crystalline polymer, crystalline hydrogenated poly (*endo*-dicyclopentadiene), was developed on the basis of the development of new cis- and iso-specific ROMP catalysts such as MoO(rac-5,5′,6,6′-Me_4-3,3′-*t*-Bu_2-2,2′-biphenolate)$_2$.

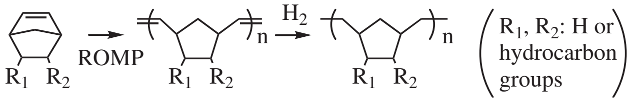
Transition-metal catalyzed polymerization is an effective means to accomplish precisely controlled polymerizations.[1] The development of metal carbene complexes such as Schrock carbenes and Grubbs carbenes has been leading stereospecific and/or living polymerizations.[2]

Zeon Corporation has been developing hydrogenated cyclic olefin polymer (COP), that is, ZEONEX® and ZEONOR®.[3] ZEONEX®, which has been commercialized since 1991, and which is a saturated COP prepared by ROMP of cyclic olefins followed by hydrogenation of double bonds (Scheme 1). This COP shows low tacticity and complete amorphous, which features high clarity and low birefringence. On the other hand, another interesting aspect is control of steric structures of COP, which may results in the development of novel COP with different physical properties from those of the amorphous COP.

In this paper, we have studied the stereospecific ROMP of cyclic olefins. In addition, hydrogenation was performed on the corresponding polymers to develop a new type of crystalline COPs. Our research has focused on the polymerization of *endo*-dicyclopentadiene (DCPD) using Schrock catalysts[4] and novel Mo and W-based stereospecific ROMP catalysts[5] (Scheme 2).

We first investigated the polymerization of DCPD using Schrock catalysts (Schrock–Hoveyda catalyst (**1**) and Mo(=*N*-2,6-*i*-Pr_2Ph)(-*O*-*t*-Bu)$_2$(=$CHMe_2$Ph) (**2**)), and successive hydrogenation of the obtained poly(DCPD)s (Table 1). The poly(DCPD) obtained from **2** exhibited no cis-selectivity, while **1** increased the cis content of the resultant poly(DCPD) up to 95%. DSC measurement suggest that the hydrogenated poly(DCPD) (H-poly(DCPD)) formed with **2** showed only a glass transition point. In sharp contrast, the insoluble H-poly(DCPD) yielded by **1** exhibited a large endothermic peak at pretty high temperature (290 °C). Moreover, the crystallinity of the corresponding H-poly(DCPD) was estimated by XRD to be about 40%.

Thus Schrock–Hoveyda catalyst (**1**) was proved to be effective for the production of crystalline H-poly(DCPD). However, from the industrial application point of view, Schrock catalyst has several disadvantages to produce crystalline H-poly(DCPD); i.e., (1) Schrock catalyst is too expensive to be used for the commercial production of plastic materials, (2) Schrock catalyst is very sensitive to air and moisture. Therefore, we decided to investigate potential of novel molybdenum(VI) and tungsten(VI) oxo bis(racemic-5,5′,6,6′-tertamethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diolate) complexes (MoO(rac-Biphenoxy)$_2$ (**3**) and WO(rac-Biphenoxy)$_2$ (**4**)) as a new class of stereospecific ROMP catalysts (Scheme 2).

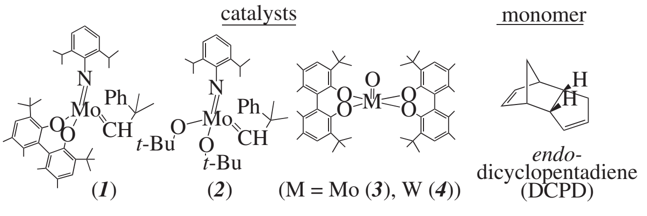


Scheme 1. Production of cycloolefin polymer (COP).

Racemic 5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-dioxy dilithium[6] (rac-Biphenoxylithium) (8.02 mmol) in diethyl ether (30 mL) was dropwise added to $MoOCl_4$ (4.01 mmol) in diethyl ether (25 mL) at −78 °C. The mixture was allowed to warm up to ambient temperature and stirred for 18 h to give a dark-blue solution. Diethyl ether was removed in vacuo and the residue was extracted with diethyl ether/*n*-hexane. The blue solution was filtered through Celite and dried in vacuo to give **3** as deep-blue microcrystals quantitatively.[6] The corresponding tungsten complex **4** was synthesized in the same manner and obtained as a deep-red powder quantitatively.[6]

Table 1 also summarizes the results of the polymerization of DCPD using **3**, **4**, and a conventional catalyst ($WOCl_4$-Et_3Al (1:1)), and successive hydrogenation of the obtained poly(DCPD)s. The complexes **3** and **4** exhibited moderate ROMP activity in the presence of *n*-BuLi as a cocatalyst.[7] The poly(DCPD), which was yielded by $WOCl_4$-Et_3Al, had low cis/trans regularity. In contrast, **3** and **4** induced the cis-specific polymerization of DCPD. The H-poly(DCPD) obtained with $WOCl_4$-Et_3Al was soluble, whereas the polymers produced by the rac-Biphenolate complexes (**3** and **4**) were entirely insoluble in usual solvents at room temperature and slightly soluble at high temperature.

The H-poly(DCPD)s were characterized by a combination of ^{13}C NMR and DSC in order to reveal the relationship between tacticity and thermal property. Tacticities of the H-poly(DCPD)s were determined by ^{13}C NMR at high temperature (150 °C) and no stereoregularity was found in the H-poly-

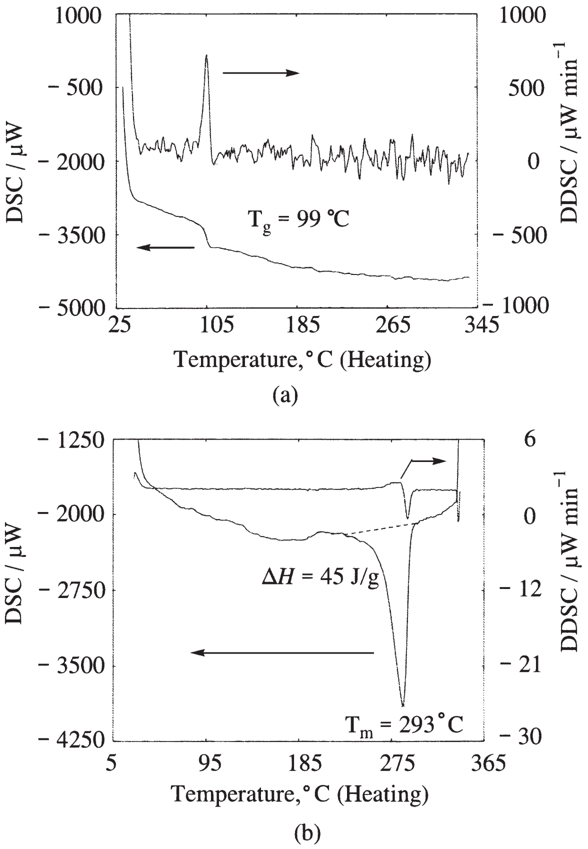


Scheme 2. ROMP catalysts and monomer in this study.

Table 1. Stereospecific ROMP of DCPD by various catalysts and hydrogenation of the obtained polymers

Catalysts	M_n^c	M_w/M_n^c	poly(DCPD)s^d		H-poly(DCPD)s^e	
			cis/trans	T_m, ΔH	Tacticity	T_m, ΔH
1^a	37000	2.8	95/5	243 °C, 14 J/g	–^{f}	290 °C, 42 J/g
2^a	75000	1.9	55/45	T_g 145 °C	58/42	T_g 100 °C
3^b	3700	2.4	85/15	263 °C, 24 J/g	95/5	293 °C, 45 J/g
4^b	3900	2.4	91/9	264 °C, 29 J/g	96/4	292 °C, 45 J/g
cf, $WOCl_4$-Et_3Al	7400	2.4	63/37	T_g 135 °C	51/49	T_g 99 °C

^{a}Polymerized in cyclohexane at 50 °C for 3 h; $[DCPD]_o = 1.3\,M$ ($1\,M = 1\,mol\,dm^{-3}$), [1-hexene] = 13 mM, [**1** or **2**] = 0.26 mM. ^{b}Polymerized in cyclohexane at 80 °C for 2 h; $[DCPD]_o = 1.3\,M$, [1-octene] = 26 mM, [**3** or **4**] = 1.3 mM, [**3** or **4**]: [*n*-BuLi] = 1:2 (mole ratio). ^{c}Before hydrogenation. ^{d}^{1}H NMR study suggested that all the poly(DCPD)s were linear polymers through selective ROMP of strained norbornene ring.[4c] ^{e}Hydrogenated in cyclohexane at 160 °C for 8 h; [poly(DCPD)] = 5 wt%, $H_2 = 1.0$ MPa, $[Ni(OAc)_2]$: [DCPD unit] = 1:100, $[Ni(OAc)_2]$:[i-Bu_3Al] = 1:4, $Ni(OAc)_2$-i-Bu_3Al hydrogenation catalyst was aged in cyclohexane at 60 °C for 15 min before the addition to poly(DCPD). ^{f}Hardly determined because the H-poly(DCPD), obtained from **1**, featured very low solubility. Its low solubility is probably due to its high molecular weight as compared to that from **3** and **4**.



(a)

(b)

Figure 1. DSC thermograms of H-poly(DCPD)s obtained with (a) $WOCl_4$-Et_3Al and (b) **3**-*n*-BuLi (1:2) on the first heating scan (determined under N_2, 10 °C/min).

(DCPD) obtained with using $WOCl_4$ as a main catalyst. It is noteworthy that the H-poly(DCPD)s formed with **3** and **4** were highly isotactic.[8] In other words, the molybdenum and tungsten biphenolate catalysts induced cis- and iso-specific ROMP of DCPD. The H-poly(DCPD) produced by $WOCl_4$-Et_3Al, having atactic polymer chain, showed a glass transition (Figure 1(a)). Great emphasis can be placed upon the fact that the insoluble H-poly(DCPD)s, which were yielded by **3** and **4**, featured large melting and small glass transition peaks (Figure 1(b) for **3**). These results clearly indicates that these insoluble H-poly(DCPD)s obtained with **3** and **4** are crystalline polymers. The thermal property of the H-poly(DCPD) obtained with $MoO(rac\text{-}Biphenoxy)_2$ (**3**) was essentially the same with that obtained with the Schrock–Hoveyda catalyst (**1**).

References and Notes

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6 rac-Biphenoxylithium: ^{1}H NMR (400.13 MHz, C_6D_6) δ 7.21(s, 2H, H_{aryl}), 2.32(s, 6H, CH_3), 1.80(s, 6H, CH_3), 1.57(s, 18H, *t*-Bu). **3**: ^{1}H NMR (400.13 MHz, C_6D_6) δ 7.24(s, 1H, H_{aryl}), 7.19(s, 1H, H_{aryl}), 2.13(s, 3H, CH_3), 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); ^{13}C NMR (100.53 MHz, C_6D_6) δ 162.7, 161.7, 137.3, 134.2, 133.7, 132.8, 132.2, 132.0, 129.7, 128.5, 125.9, 124.7, 35.3, 34.8, 32.1, 31.3, 20.5, 20.3, 16.7, 16.6; Found: C, 70.01; H, 7.98; Mo, 11.40%. Calcd for $MoC_{48}H_{64}O_5$: C, 70.57; H, 7.90; Mo, 11.74%. **4**: ^{1}H NMR (400.13 MHz, C_6D_6) δ 7.26(s, 1H, H_{aryl}), 7.19(s, 1H, H_{aryl}), 2.13(s, 3H, CH_3), 2.03(s, 3H, CH_3), 1.68(s, 3H, CH_3), 1.66(s, 3H, CH_3), 1.55(s, 9H, *t*-Bu), 1.44(s, 9H, *t*-Bu); ^{13}C NMR (100.53 MHz, C_6D_6) δ 158.3, 158.0, 137.5, 134.7, 133.9, 133.1, 132.6, 131.3, 129.6, 127.5, 127.0, 125.3, 35.3, 34.6, 32.2, 31.2, 20.5, 20.1, 16.9, 16.8; Found: C, 62.28; H, 7.10%. Calcd for $WC_{48}H_{64}O_5$: C, 63.71; H, 7.13%.

7 The initiation mechanism can be speculated as follows: Reaction of $MoO(rac\text{-}Biphenoxy)_2$ with two-fold of *n*-BuLi may generate unstable dialkyl molybdenum species $(n\text{-}C_4H_9)_2Mo(=O)(rac\text{-}Biphenoxy)$. Then the *n*-butyl group on the Mo becomes an *n*-butylidene by α-H elimination. It is plausible that the above-stated molybdenum *n*-butylidene, $n\text{-}C_3H_7CH=Mo(=O)(rac\text{-}Biphenoxy)$, induces the present cis- and iso-specific ROMP.

8 Thus far, microstructure of H-poly(DCPD) had been studied in detail (J. G. Hamilton, K. J. Ivin, and J. J. Rooney, *J. Mol. Catal.*, **36**, 115 (1986).). Signal splittings owing to tacticity had been observed in polymer, however, its assignment of signals to m and r dyads had not been verified in the ^{13}C NMR spectra. According to the combination of our NOESY study and our MOPAC simulation, the signal at 43.35 ppm can be assigned to m dyad, and 44.25 ppm is to r dyad. Therefore, we concluded that the present catalyst systems promote iso-specific polymerization.

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