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Scandium-Catalyzed Regio- and Stereospecific *cis*-1,4-Polymerization of 1,3-Cyclohexadiene and Copolymerization with Ethylene

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ABSTRACT: In the presence of an activator such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$, the half-sandwich scandium dialkyl complexes $Cp'Sc(CH_2SiMe_3)_2(THF)$ (Cp' = $C_5Me_4SiMe_3$ (**1**), C_5Me_5 (**2**), $C_5H_3(SiMe_3)_2$ (**3**)) showed excellent regio- and stereoselectivity for the polymerization of 1,3-cyclohexadiene (CHD) and its copolymerization with ethylene. The homopolymerization of CHD afforded soluble crystalline *cis*-1,4-linked poly(CHD)s with very high stereoselectivity (tacticity up to 99 mol %). The copolymerization of CHD with ethylene gave the corresponding copolymers with a wide range of CHD contents (10−67 mol %) in a regio- and stereospecific 1,4-*cis* fashion.

Introduction

1,3-Cyclohexadiene (CHD)-based polymers are of much interest from both scientific and practical perspective, because the presence of six-membered rings in the main polymer chain is expected to bring high mechanical strength and thermal stability, and moreover, chemical modification or functionalization of the residual C−C double bonds in the cyclic structure could lead to formation of a new family of high-performance polymer materials.[1−9] A variety of initiators/catalysts were reported to effect the polymerization of CHD, but few were regio- and stereospecific, because CHD can be polymerized in several different patterns in terms of 1,2- and 1,4-regioselectivity and *cis*- and *trans*-stereoselectivity. The polymerization of CHD by radicals,[1] anions,[2,3] cations,[4] or Ziegler−Natta catalysts[5] usually gave amorphous poly(CHD)s containing a mixture of 1,2- and 1,4-CHD units without stereoregularity. Nickel-based catalysts were reported to show high regio- and stereoselectivity, but the resulting polymers are insoluble in common organic solvents and show melting points close to their decomposition temperatures (> 300 °C), which thus makes them difficult to process and characterize by NMR and GPC analyses.[6]

The copolymerization of CHD with other olefin monomers such as ethylene is expected to yield CHD-based cyclic olefin copolymers which may show improved properties.[7,9] However, very few catalysts were known to effect CHD−ethylene copolymerization, because catalysts active for ethylene polymerization can be poisoned by a conjugated diene such as CHD. The only precedent CHD−ethylene copolymerization was achieved by Ti-based catalysts albeit with relatively low CHD incorporation in most cases.[7] The use of rare-earth catalysts for the polymerization and copolymerization of CHD has remained almost unexplored.[10]

We recently reported that scandium-based catalysts can show excellent activity and selectivity for the polymerization and copolymerization of a wide range of olefin monomers,[11,12] including the alternating and random copolymerization of a conjugated diene such as isoprene with ethylene,[12j] random copolymerization of isoprene with norbornene,[12g] and syndiospecific copolymerization of styrene with isoprene.[12f] We report here the regio- and stereospecific *cis*-1,4-polymerization and copolymerization of CHD with ethylene by the half-sandwich scandium catalysts, which afforded for the first time soluble crystalline *cis*-1,4-poly(CHD)s with tacticity up to 99% and CHD-ethylene copolymers with a wide range of CHD contents (10−67 mol %) and almost perfect *cis*-1,4-regularity.

Experimental Section

General Methods. All manipulations of air- and moisture-sensitive compounds were performed under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 1 ppm. Anhydrous THF, hexane and toluene were refluxed and distilled from sodium/benzophenone under dry nitrogen, and degassed by the freeze−pump−thaw cycles, and dried over fresh Na chips in the glovebox. 1,3-Cyclohexadiene (CHD) was purchased from TCI, dried over CaH_2, vacuum-transferred, and degassed by two freeze−pump−thaw cycles. Ethylene (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation and used without purification. $ScCl_3$ was purchased from Strem. $LiCH_2SiMe_3$ (1.0 M solution in pentane), $C_5Me_4H(SiMe_3)$, $C_5H_4(SiMe_3)_2$-1,3, and C_5Me_5H were purchased from Aldrich, and used as received. $[Cp'Sc(CH_2SiMe_3)_2(THF)]$ (Cp' = $C_5Me_4SiMe_3$ (**1**), C_5Me_5 (**2**), $C_5H_3(SiMe_3)_2$-1,3 (**3**) were synthesized as described previously.[12b,j] The deuterated solvents 1,2-dichlorobenzene-d_4 (99 atom % D), chloroform-d_1 (99.8 atom % D) and 1,1,2,2,-tetrachloroethane-d_2 (99.6 atom % D) were obtained from Cambridge Isotope.

The NMR data of the homopolymers of CHD and the copolymers of ethylene and CHD were obtained on a JEOL JNM-EX 270 (FT, 300 MHz for ^1H; 75.5 MHz for ^{13}C) spectrometer at

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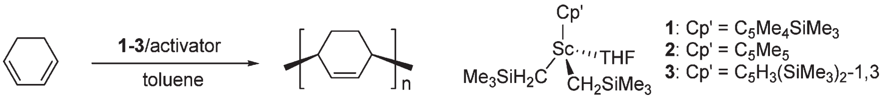
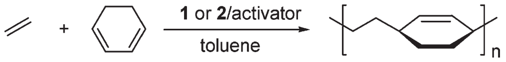
Table 1. Polymerization of 1,3-Cyclohexadiene (CHD) by Half-Sandwich Scandium Catalysts[a]



entry	comp (μmol)	activator[b]	T (°C)	yield (g)	convn (%)	activity[c]	1,4-poly(CHD) isomers (mol %)[d] *trans*	*cis*	*tac.*	M_n[e] (10^3)	M_w/M_n[e]	T_m[f] (°C)
1	**1** (40)		25									
2[g]		**A**	25	0.80[h]	100	1200	72	28		1.9[i]	2.17[i]	144
3	**1** (40)	**A**	25	0.44	55	3.7	1	99	77	1.5	2.46	223
4	**1** (40)	**B**	25	0.19	24	1.6	1	99	83	4.2	2.84	231
5	**1** (40)	**C**	25	trace								
6	**1** (67)	**A**	25	0.65	81	3.2	1	99	77	4.6	1.99	224
7	**1** (100)	**A**	25	0.80	100	2.7	1	99	80	5.1	1.88	224
8[j]	**1** (40)	**A**	0	0.14	18	0.3	1	99	93	2.5	2.12	225
9[j]	**1** (40)	**A**	−10	0.09	11	0.2	0	99	99	2.9	2.10	225
10	**2** (40)	**A**	25	0.34	43	2.8	0	99	99	3.6	2.88	221
11	**2** (40)	**B**	25	0.16	20	1.3	0	99	99	3.8	3.67	221
12	**3** (40)	**A**	25	0.56[k]	70	4.7	32	68		2.2[i]	1.58[i]	169

[a] Conditions: [Sc]/[activator] = 1:1, CHD = 10 mmol, solvent = toluene, V = 5 mL, and t = 3 h, unless otherwise noted. [b] Activator: **A** = $[Ph_3C][B(C_6F_5)_4]$, **B** = $[PhMe_2NH][B(C_6F_5)_4]$, and **C** = $B(C_6F_5)_3$. [c] Activity: kg of polymer/($Sc_{mol}\cdot h$). [d] Determined by ^1H,^{13}C NMR. The tacticity (*tac*, either isotactic or syndiotactic) of 1,4-poly(CHD) was determined by the integration ratio of the ^{13}C NMR signal at 39.42 to that at 39.64 ppm, but whether it is isotactic or syndiotactic was not unambiguously identified. [e] Determined by GPC in *o*-dichlorobenzene at 120 °C against polystyrene standard. [f] Measured by DSC. [g] t = 1 min. [h] 1,4-poly(CHD)/1,2-poly(CHD) = 75/25. [i] Determined by GPC in THF at 40 °C against polystyrene standard. [j] t = 12 h. [k] 1,4-Poly(CHD)/1,2-poly(CHD) = 89/11.

Table 2. Regio- and Stereospecific Copolymerization of 1,3-Cyclohexadiene (CHD) with Ethylene (E) by Half-Sandwich Scandium Catalysts[a]



entry	comp.	CHD (mmol)	E/CHD (M/M)[b]	T (°C)	yield (g)	activity[c]	CHD cont.[d] (mol %)	M_n[e] (10^3)	M_w/M_n[e]	T_m[f] (°C)
1[g]	**1**	0.0	-	25	1.40	1050	0	103.5	1.80	131
2[h]	**1**	10.0	-	25	0.44	3.7	100	1.5	2.46	223
3	**1**	5.0	1/5.0	25	1.31	393	10	105.8	1.54	118
4	**1**	6.3	1/6.3	25	0.87	261	26	49.8	1.66	124
5	**1**	7.5	1/7.5	25	0.35	105	39	44.0	1.37	126
6	**1**	10.0	1/10.0	25	0.29	87	42	33.8	1.36	126
7	**1**	12.5	1/12.5	25	0.15	45	46	27.1	1.31	124
8	**1**	15.0	1/15.0	25	0.08	24	51	2.5	1.67	126
9	**1**	25.0	1/25.0	50	0.20	60	67	3.0	1.65	128
10	**1**	10.0	1/10.0	0	0.12	36	29	90.9	1.68	130
11	**2**	10.0	1/10.0	25	0.69	207	40	27.6	2.21	123
12	**2**	15.0	1/15.0	25	0.24	72	50	7.0	1.98	126

[a] Conditions: Sc = 40 μmol, Sc/$[Ph_3C][B(C_6F_5)_4]$ = 1/1 (molar ratio), $P_{ethylene}$ = 1 atm, solvent = toluene, V = 40 mL, and t = 5 min, unless otherwise noted. [b] Estimated on the basis that the ethylene solubility in toluene is about 2 g/L under an atmosphere pressure. [c] kg of copolymer/($Sc_{mol}\cdot h\cdot atm$). [d] Determined by ^1H NMR. [e] Determined by GPC in *o*-dichlorobenzene at 120 °C against polystyrene standard. [f] Measured by DSC. [g] Ethylene homopolymerization: t = 2 min. [h] CHD homopolymerization under an atmosphere of N_2: V = 5 mL, t = 3 h.

120 or 50 °C, respectively, with 1,1,2,2-$C_2D_2Cl_4$ or $CDCl_3$ as a solvent. The molecular weights and the molecular weight distributions of CHD homopolymers and ethylene/CHD copolymers were determined at 120 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by use of polystyrene standard EasiCal PS-1 (PL Ltd.). The DSC measurements were performed on a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 350 °C, cooling at 20 °C/min to −10 °C, and then recording the second DSC scan.

Typical Procedure for the Polymerization of CHD (Table 1, Entry 3). In a glovebox, a toluene solution (3 mL) of $[Ph_3C][B(C_6F_5)_4]$ (37 mg, 40 μmol) was added to a toluene solution (2 mL) of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (19 mg, 40 μmol) in a 100 mL flask. The mixture was stirred at room temperature for a few minutes, and 0.8 g of 1,3-cyclohexadiene (10 mmol) was added under vigorous stirring. After 3 h, the flask was taken outside of the glovebox. The mixture was poured into methanol (200 mL, containing 1% butylhydroxytoluene (BHT)) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried *in vacuo* at 60 °C to a constant weight (0.44 g, 55%). The polymer product is soluble in dichlorobenzene and 1,1,2,2-tetrachloroethane at 120 °C.

Typical Procedure for the Copolymerization of Ethylene and CHD (Table 2, Entry 6). In a glovebox, a toluene solution (15 mL) of 1,3-cyclohexadiene (0.8 g, 10.0 mmol) was charged into a two-necked flask with a stirring bar. The flask was taken outside, set in a water bath (25 °C), and connected to a well-purged Schlenk ethylene line and a mercury-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 1 min. A toluene solution (5 mL) of the catalyst generated by reaction of $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (19 mg, 40 μmol) with $[Ph_3C][B(C_6F_5)_4]$ (37 mg, 40 μmol) as described above was then added through a syringe under vigorous stirring. The polymerization was quenched after 5 min by addition of methanol (200 mL, containing 1% butylhydroxytoluene (BHT)). The polymer product was collected by filtration, washed with methanol, and then dried *in vacuo* at 60 °C to a constant weight (0.29 g, 87 kg of copolymer/(mol of Sc·h·atm)). The polymer product is soluble in dichlorobenzene and 1,1,2,2-tetrachloroethane at 120 °C. The CHD content of the copolymer was calculated according to the following formula:

$$\text{mol CHD\%} = \{(2I_{5.4-5.7\,\text{ppm}}) \div (I_{1.0-1.8\,\text{ppm}})\} \times 100\%$$

where $I_{5.4-5.7\,\text{ppm}} = 2\text{H}_{\text{CHD}}$ is the peak area of unsaturated olefinic protons of CHD units at 5.4−5.7 ppm and $I_{1.0-1.8\,\text{ppm}} = 4\text{H}_{\text{CHD}} + 4\text{H}_{\text{Ethy}}$ is the total peak area of methylene protons at 1.0−1.8 ppm in the ^{1}H NMR spectrum.

Results and Discussion

Homopolymerization of 1,3-Cyclohexadiene (CHD). Some representative results of the homopolymerization of CHD under various conditions are summarized in Table 1. The neutral scandium dialkyl complexes **1**−**3** showed no activity in the absence of an activator (Table 1, entry 1). The trityl perfluorophenylborate [Ph_3C][$B(C_6F_5)_4$] (**A**) alone was active, but yielded amorphous poly(CHD) with mixed 1,2- and 1,4-*cis*/*trans* microstructures, similar to other cationic initiators reported previously (Table 1, entry 2).[4] [$PhMe_2NH$][$B(C_6F_5)_4$] (**B**) and $B(C_6F_5)_3$ (**C**) were inactive for CHD polymerization under the same conditions. In contrast, the combination of **1** and [Ph_3C][$B(C_6F_5)_4$] (**A**) exhibited excellent regio- and stereoselectivity for the polymerization of CHD, affording exclusively the *cis*-1,4-linked poly(CHD) at room temperature (1,4-selectivity: 100%, *cis*-selectivity: 99%, tacticity: 77%) (Table 1, entry 3). As an activator, [$PhMe_2NH$][$B(C_6F_5)_4$] (**B**) was also effective for the regio- and stereosefic polymerization of CHD, albeit with a lower activity (Table 1, entry 4). $B(C_6F_5)_3$ (**C**) was almost inert under the same conditions (Table 1, entry 5). When the polymerization by **1**/**A** was carried out at lower temperatures, further higher stereoselectivity was observed (Table 1, entries 3, 8−9). At −10 °C, only one single stereoisomer was obtained (1,4-selectivity: 100%, *cis*-selectivity: 99%, tacticity: 99%), as shown by the ^{1}H and ^{13}C NMR analyses (*vide infra*) (Table 1, entry 9). The C_5Me_5-supported complex **2** also showed high 1,4-*cis* regio- and stereoselectivity under similar conditions (Table 1, entries 10 and 11). The less sterically demanding complex **3** showed much lower regio- and stereoselectivity, though it showed higher activity than that of **1** and **2** under the same conditions (Table 1, entry 12).

The poly(CHD)s prepared by use of the Sc catalysts **1** and **2** showed endothermal melting points (T_m) around 221−231 °C (Table 1) and clear peaks in the powder X-ray diffraction (XRD) spectra (see Supporting Information), suggesting that these polymers are crystalline polymers.[6b,13,14] Remarkably, these crystalline polymers are soluble in $C_2H_2Cl_4$ and *o*-$C_6H_4Cl_2$ at 120 °C and can thus be characterized by NMR analyses. The ^{1}H and ^{13}C NMR spectra of some representative poly(CHD) samples with different microstructures are shown in Figures 1 and 2, respectively. The ^{1}H NMR signals at 5.5−5.8, 1.9−2.4, and 1.2−1.8 ppm can be assigned to the olefinic protons (Ho), the allylic protons (Ha), and the aliphatic protons (Hb), respectively (Figure 1).[15] Because 1,2-poly(CHD) units should show an area ratio of 2:3:3 for the olefinic, allylic, and aliphatic proton peaks and 1,4-poly(CHD) units should give a ratio of 2:2:4 for the same peaks, it is not difficult to estimate the content of the 1,2- and 1,4-units in the polymer from the ^{1}H NMR spectra. In 1,4-poly(CHD) units, the *cis*-isomer could show a single peak at 1.60 ppm for the aliphatic protons (Hb), while the *trans*-isomer would give two peaks at 1.35 and 1.75 ppm, respectively.[15] The ^{1}H NMR peaks of the olefinic, allylic, and aliphatic protons in the polymer prepared by **1**/[Ph_3C][$B(C_6F_5)_4$] at either 25 °C (Figure 1c) or −10 °C (Figure 1d) showed an area ratio of 1:1:2 (or 2:2:4), suggesting that the CHD units in these polymers are solely in a 1,4-form. In addition, only a single peak was observed at 1.6 ppm for the aliphatic protons (Hb) in these polymers. These results suggest that the CHD units in these polymers should be exclusively 1,4-*cis*-linked.[15] In contrast, the poly(CHD)s prepared by [Ph_3C][$B(C_6F_5)_4$] (Figure 1a) and **3**/[Ph_3C][$B(C_6F_5)_4$] (Figure 1b) consist of mixed *cis*-/*trans*- 1,2 and 1,4 microstructures as shown by the ^{1}H NMR spectra.

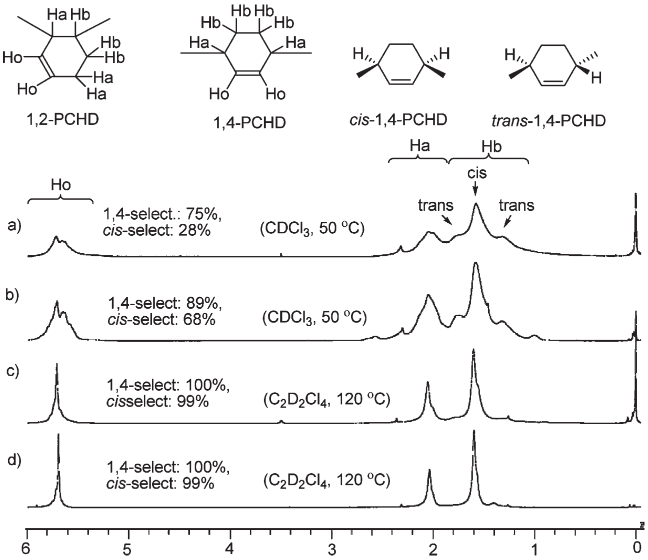


Figure 1. ^{1}H NMR spectra of poly(CHD)s with different microstructures prepared by use of (a) [Ph_3C][$B(C_6F_5)_4$] (entry 2), (b) **3**/[Ph_3C][$B(C_6F_5)_4$] (entry 12), (c) **1**/[Ph_3C][$B(C_6F_5)_4$] at 25 °C (entry 3), and (d) **1**/[Ph_3C][$B(C_6F_5)_4$] at −10 °C (entry 9), as shown in Table 1.

The ^{13}C NMR spectra of poly(CHD)s synthesized by **1**/[Ph_3C][$B(C_6F_5)_4$] (Figures 2c, d) also demonstrated the extremely high *cis*-1,4-regularity of these polymers.[15] In the polymer obtained at −10 °C (Figure 2d), the methine carbon atoms (C3 and C6) showed a sharp singlet at 39.9 ppm, suggesting that this polymer consists of a single regio- and stereoisomer. Unfortunately, however, a specific tacticity (whether isotactic or syndiotactic) in this polymer was not unequivocally identified because of the lack of authentic data for comparison.

Copolymerization of 1,3-Cyclohexadiene (CHD) with Ethylene. Complexes **1** and **2** were chosen to examine the copolymerization of CHD with ethylene (Table 2). In the presence of **1**/[Ph_3C][$B(C_6F_5)_4$] in toluene, the copolymerization of CHD with ethylene took place rapidly to give the corresponding CHD−ethylene copolymers. When the CHD monomer feed was raised under 1 atm of ethylene, more CHD was incorporated into the copolymers (up to 67 mol %) (Table 2, entries 3−9).[7] Under the same conditions, complex **2** displayed higher activity than that of **1**, but both complexes showed similar CHD incorporation ability (Table 2, entries 11 and 12 vs 6 and 8).

The copolymers obtained above are soluble in $C_2H_2Cl_4$ and *o*-$C_6H_4Cl_2$ at 120 °C. The GPC curves of the copolymers are all unimodal with moderate molecular weight distributions (1.31−2.21), suggesting the predominance of a homogeneous single-site catalyst species. The ^{1}H NMR spectra of the copolymers showed a 1:1 area ratio for the olefinic proton signals around 5.60 ppm and the allylic proton signals around 1.97 ppm, suggesting that the CHD units in the copolymers are solely in a 1,4-form regardless of the CHD content (see Figure 3). This is in consistence with the high regioselectivity observed above in the homopolymerization of CHD.

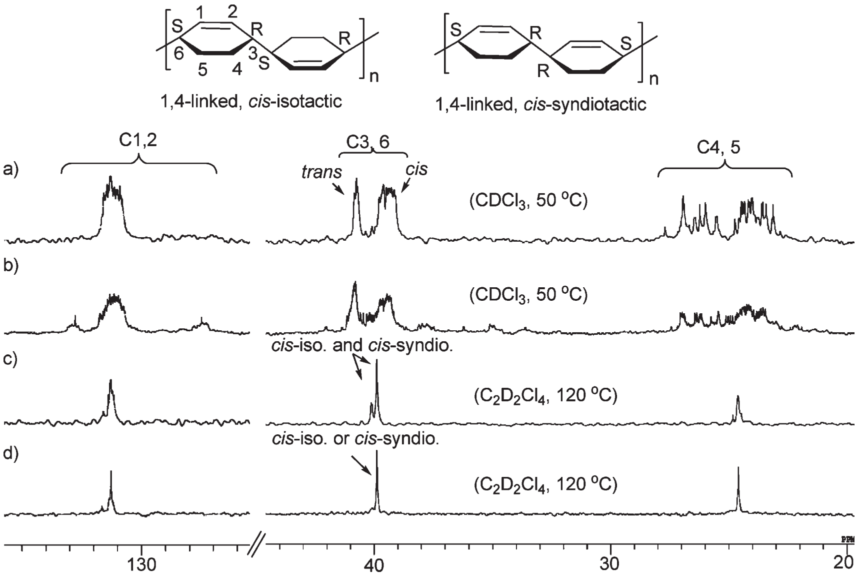


Figure 2. ^{13}C NMR spectra of poly(CHD)s with different microstructures prepared by use of (a) $[Ph_3C][B(C_6F_5)_4]$ (entry 2), (b) **3**/$[Ph_3C][B(C_6F_5)_4]$ (entry 12), (c) **1**/$[Ph_3C][B(C_6F_5)_4]$ at 25 °C (entry 3), and (d) **1**/$[Ph_3C][B(C_6F_5)_4]$ at −10 °C (entry 9), as shown in Table 1.

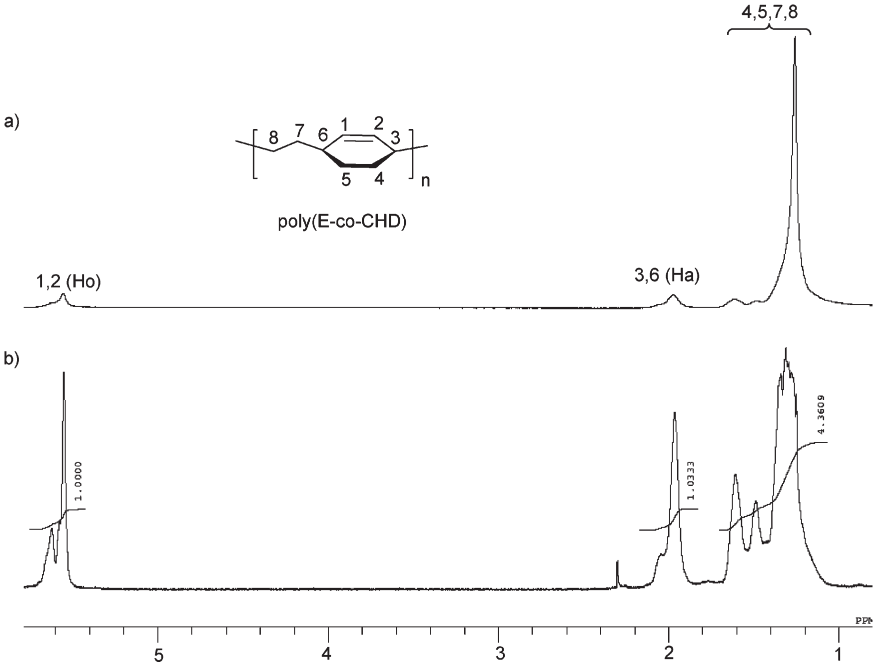


Figure 3. ^{1}H NMR spectra of poly(ethylene-*co*-CHD)s with (a) CHD content = 10 mol % (Table 2, entry 3) and (b) CHD content = 46 mol % (Table 2, entry 7).

The ^{13}C NMR spectra of the CHD−ethylene copolymers with lower CHD contents were less complicated than those with higher CHD contents, but both suggest that the CHD units in the copolymers have high *cis*-1,4 regio- and stereoregularity. As shown in Figure 4a, the CHD units in the copolymer with 10 mol % of CHD are distributed predominantly in an isolated state, while small amounts of alternating ethylene−CHD sequences and CHD−CHD sequences are also observed.[7a,16] In the copolymer containing 46 mol % of CHD (Figure 4b), the alternating ethylene−CHD sequences and CHD−CHD diad and triad sequences increased significantly, while long ethylene blocks (longer than three successive ethylene units) could be negligible.

The CHD−ethylene copolymers showed melting points at 118−130 °C, which were not so much affected by increasing CHD incorporation. The melting point first decreased at low CHD content from 131 °C (homo-PE) to 118° at 10 mol % of inserted CHD (Table 2, entry 3). This is in good agreement with the NMR observation that isolated CHD units are predominant in this copolymer, which may disturb the crystallization of ethylene sequences. By increasing the CHD content to 26 mol %, T_m increased to reach 124 °C, and then remained almost constant (slowly increased to 128 °C, when the CHD content was raised from 26 mol % to 67 mol %, Table 2 entries 4−9). Higher melting temperatures (or closer to that of homopoly(CHD), ca. 230 °C) were not reached at high CHD content. These results could be due to the lack of long CHD blocks in the present copolymers; note that CHD blocks with more than four successive CHD units were not observed even at 67 mol % of CHD content. These results are

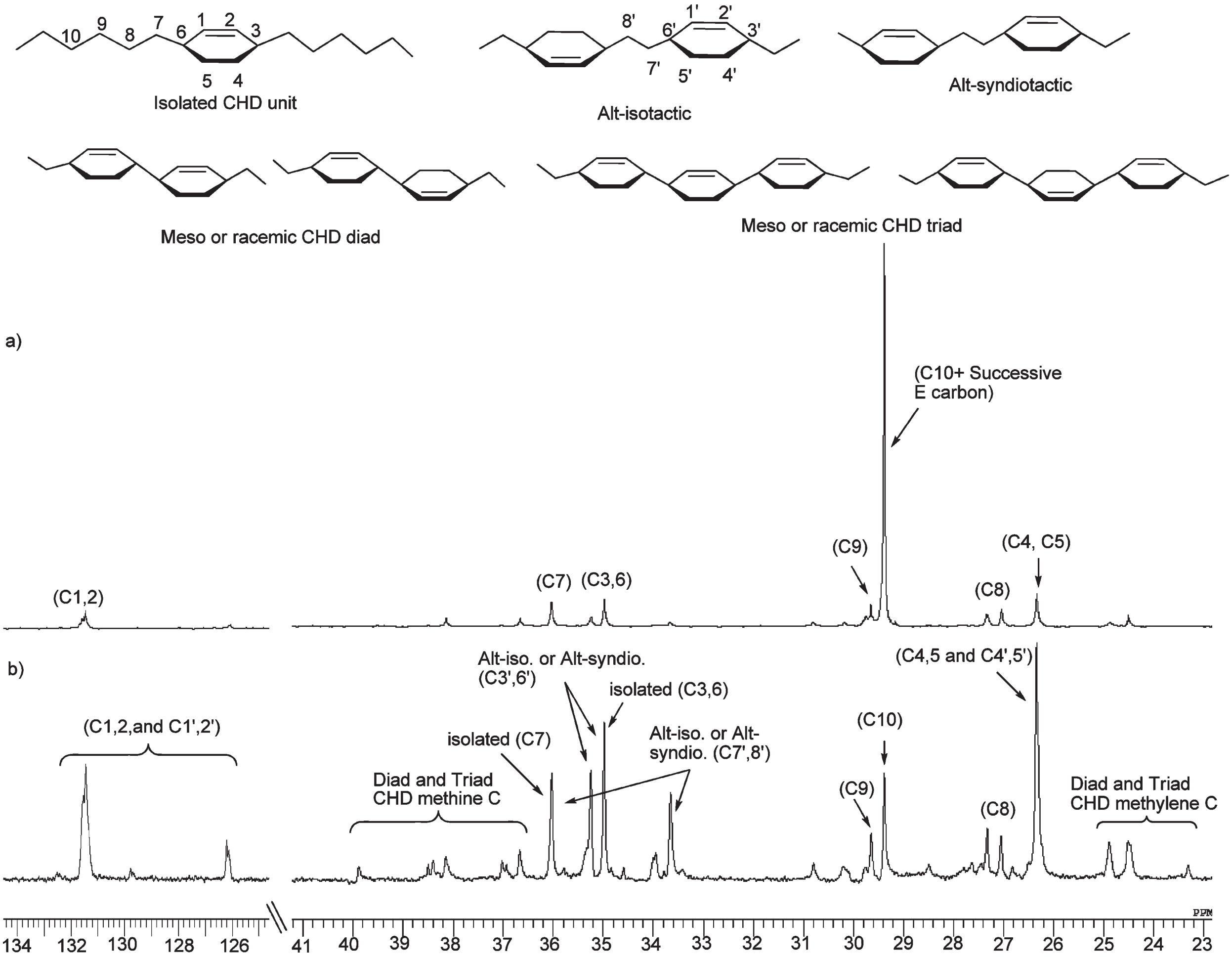


Figure 4. ^{13}C NMR spectra of poly(ethylene-*co*-CHD)s with (a) CHD content = 10 mol % (Table 2, entry 3) and (b) CHD content = 46 mol % (Table 2, entry 7).

also in agreement with the fact that the CHD polymerization activity of the present catalyst is much lower than that of the ethylene polymerization, which would thus hamper the formation of long CHD blocks.[17]

Conclusion

By use of a combination of the half-sandwich scandium dialkyl complexes such as **1** and **2** with an appropriate activator such as $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$, the regio- and stereospecific 1,4-*cis* polymerization of 1,3-cyclohexadiene (CHD) and copolymerization with ethylene have been achieved, which afforded for the first time soluble crystalline *cis*-1,4-linked poly(CHD)s with tacticity up to 99% and random CHD-ethylene copolymers with a wide range of CHD contents and almost perfect *cis*-1,4 regularity. These results suggest that the cationic half-sandwich scandium alkyl species can show unique activity for the polymerization of cyclic dienes. Further studies on the polymerization and copolymerization of related olefin monomers are in progress.

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Supporting Information Available: Figures showing XRD, GPC, DSC, and NMR (^{1}H and ^{13}C) spectra of representative polymer products. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Stücklen, H.; Thayer, H.; Willis, P. *J. Am. Chem. Soc.* **1940**, *62*, 1717–1719.

(2) (a) Cassidy, P. E.; Marvel, C. S.; Ray, S. *J. Polym. Sci.* **1965**, *A3*, 1553–1565. (b) Lussi, H.; Braman, J. *Helv. Chim. Acta* **1967**, *50*, 1233–1243. (c) Sharaby, Z.; Jagur-Grodzinski, J.; Martan, M.; Vofsi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 901–915. (d) Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743–2753.

(3) (a) Natori, I. *Macromolecules* **1997**, *30*, 3696–3697. (b) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982–987. (c) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 4687–4694. (d) Hong, K. L.; Mays, J. W. *Macromolecules* **2001**, *34*, 782–786. (e) Wiliamson, D. T.; Elman, J. F.; Masison, P. H.; Pasquale, A. J.; Long, T. E. *Macromolecules* **2001**, *34*, 2108–2114. (f) Williamson, D. T.; Glass, T. E.; Long, T. E. *Macromolecules* **2001**, *34*, 6144–6146. (g) Quirk, R. P.; You, F.; Zhu, L.; Cheng, S. Z. D. *Macromol. Chem. Phys.* **2003**, *204*, 755–761. (h) Quirk, R. P.; You, F.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2004**, *37*, 1234–1242. (i) Williamson, D. T.; Buchanan, T. D.; Elkins, C. L.; Long, T. E. *Macromolecules* **2004**, *37*, 4505–4511. (j) Natori, I.; Natori, S. *J. Polym, Sci., Part A: Polym. Chem.* **2008**, *46*, 6604–6611. (k) Natori, I.; Natori, S.; Ogino, K. *Macromolecules* **2009**, *42*, 1964–1969.

(4) (a) Frey, D. A.; Hasegawa, M.; Marvel, C. S. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1963**, *1*, 2057–2065. (b) Lefebvre, G.; Dawans, F. *J. Polym, Sci., Part A: Polym. Chem. Ed.* **1964**, *2*, 3277–3295.

(5) (a) Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* **1959**, *81*, 448–452. (b) Yousufzi, A. H. K.; End, V.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1601–1605.

(6) (a) Dolgoplosk, A.; Beilin, S. I.; Korshak, Y. V.; Chernenko, G. M.; Vardanyan, L. M.; Teterina, M. P. *Eur. Polym. J.* **1973**, *9*, 895–908. (b) Nakano, M.; Yao, Q.; Usuki, A.; Tanimura, S.; Matsuoka, T. *Chem. Commun.* **2000**, 2207–2208. (c) Longo, P.; Freda, C.; Ballesteros, O. R.; Grisi, F. *Macromol. Chem. Phys.* **2001**, *202*, 409–412.

(7) (a) Heiser, D. E.; Okuda, J.; Gambarotta, S.; Mülhaupt, R. *Maromol. Chem. Phys.* **2005**, *206*, 195–202. (b) Heiser, D. E.; Pelascini, F.; Kramer, D.; Scott, J.; Gambarotta, S.; McCahill, J.; Stephan, D. W.; Okuda, J.; Mülhaupt, R. *Macromol. Symp.* **2006**, *236*, 156–160.

(8) Natori, I.; Sato, H. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 837–845 and references therein .

(9) For a recent review on the copolymerization of cyclic olefins, see: Li, X.; Hou, Z. *Coord. Chem. Rev.* **2008**, *252*, 1842–1869.

(10) We have previously communicated the *cis*-1,4-selective homopolymerization of CHD by cationic rare earth metal polyhydrido complexes. See: Li, X.; Baldamus, J.; Nishiura, M.; Tardif, O.; Hou, Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 8184–8188.

(11) A recent review: Nishiura, M.; Hou, Z. *Nature Chem.* **2010**, *2*, 257–268.

(12) (a) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910–13911. (b) Li, X.; Baldamus, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 962–965. (c) Li, X.; Hou, Z. *Macromolecules* **2005**, *38*, 6767–6768. (d) Hou, Z.; Luo, Y.; Li, X. *J. Organomet. Chem.* **2006**, *691*, 3114–3121. (e) Li, X.; Nishiura, M.; Mori, K.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2007**, 4137–4139. (f) Zhang, H.; Luo, Y.; Hou, Z. *Macromolecules* **2008**, *41*, 1064–1066. (g) Yu, N.; Nishiura, M.; Li, X.; Xi, Z.; Hou, Z. *Chem. Asian J.* **2008**, *3*, 1406–1414. (h) Nishiura, M.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2008**, 2019–2021. (i) Fang, X.; Li, X.; Hou, Z.; Assoud, J.; Zhao, R. *Organometallics* **2009**, *28*, 517–522. (j) Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 13870–13882. (k) Takimoto, T.; Usami, S.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 18266–18268.

(13) Tanimura, S.; Matsuoka, T.; Nakano, M.; Usuki, A. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 973–978.

(14) The DSC traces of the poly(CHD)s all showed an endothermic peak around 230 °C at the first heating, but it was very difficult to find the endothermic peak at the second heating, which may indicate the difficulty of crystallization of these homopolymers.

(15) Sharaby, Z.; Martan, M.; Jagur-Grodzinski, J. *Macromolecules* **1982**, *15*, 1167–1173.

(16) The ^{13}C NMR assignments of the CHD−ethylene copolymers were confirmed by ^{1}H-^{1}H COSY and ^{13}C-DEPT experiments. See Supporting Information for details.

(17) Similar phenomenon was observed previously in ethylene−norbornene copolymerization. See refs 12b, 12c.