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Scandium-Catalyzed Cyclocopolymerization of 1,5-Hexadiene with Styrene and Ethylene: Efficient Synthesis of Cyclopolyolefins Containing Syndiotactic Styrene—Styrene Sequences and Methylene-1,3-cyclopentane Units

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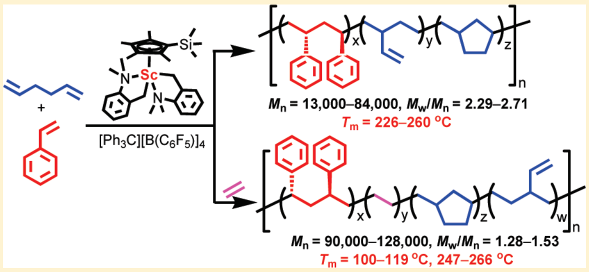
Supporting Information

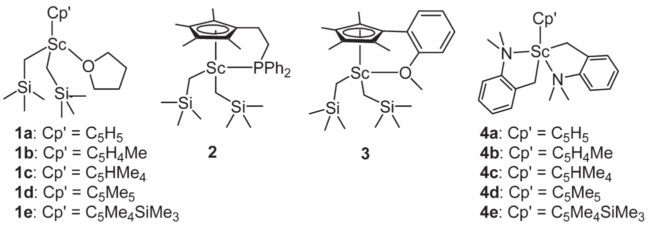
ABSTRACT: The polymerization of 1,5-hexadiene (HD) and its copolymerization with styrene and ethylene by a series of half-sandwich scandium dialkyl complexes bearing various auxiliary ligands have been examined. Significant ligand influence on the catalytic activity and selectivity has been observed. The THF-free aminobenzyl scandium complex with a sterically demanding ligand, such as $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**4e**), in combination with an equivalent of $[Ph_3C][B(C_6F_5)_4]$, serves as an excellent catalyst for the cyclocopolymerization of HD with styrene to afford a new family of polymer materials containing methylene-1,3-cyclopentane (MCP) units, vinyltetramethylene (VTM) units, and unique syndiotactic styrene—styrene sequences. By use of this catalyst, the terpolymerization of HD, styrene, and ethylene has also be achieved for the first time to afford novel cyclopolymer materials containing the five-member ring MCP units, ethylene—ethylene blocks, and syndiotactic styrene—styrene sequences. The composition of the copolymers can be controlled in a wide range simply by changing the comonomer feeding ratios. Most of the resulting copolymers show high melting points originating from the syndiotactic polystyrene blocks and polyethylene blocks well as in the case of the terpolymers.



INTRODUCTION

The creation of novel polymer materials having desired structures and properties relies significantly on the development of new generations of polymerization catalysts. The cyclopolymerization of 1,5-hexadiene (HD) is a convenient method for the preparation of cyclopolyolefins containing the five-member ring methylene-1,3-cyclopentane (MCP) units that may bring useful mechanical and optical properties.[1,2] So far, a large number of catalysts based on various metals such as Ti,[3] Zr,[4] Y,[5] Sm,[6] and V[7] have been reported for the homopolymerization of HD. However, catalysts suitable for the copolymerization of HD with other monomers are rather limited.[3e,7−9] Previously, group 4 metal-based catalysts were reported to effect the copolymerization of HD with ethylene or propylene,[3e,8,9] but attempts to terpolymerize HD with ethylene and styrene by a group 4 metal catalyst yielded a polymer product with maximum incorporation of styrene in only 2.1 mol %.[8a] The potential of rare-earth catalysts in the copolymerization of HD has remained almost unexplored.

Chart 1. Half-Sandwich Scandium Complexes with Different Cyclopentadienyl and Alkyl Ligands



We have recently reported that half-sandwich scandium—alkyl complexes such as $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ (**1e**, Chart 1) and $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**4e**) can serve as excellent catalysts for the polymerization and copolymerization of a wide range of olefins,[10,11] such as the syndiospecific copolymerization of styrene with ethylene,[11a,j] isoprene,[11e] or caprolactone[11h] and the terpolymerization of styrene, ethylene, and 1,6-heptadiene[11i] to give the corresponding copolymers showing unique mechanical and physical properties because of incorporation of semicrystalline syndiotactic styrene—styrene

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sequences.[12,13] In this study, we have examined the potential of the half-sandwich scandium catalysts bearing various cyclopentadienyl ligands and different alkyl ligands (Chart 1) for the polymerization of HD and its copolymerization with styrene and ethylene. By use of an appropriate ligand combination, the copolymerization of HD with styrene and the terpolymerization of HD with styrene and ethylene have been achieved for the first time to give a new family of cyclopolyolefins containing unique syndiotactic styrene−styrene sequences, MCP five-member ring units, and vinyl branch units.

EXPERIMENTAL SECTION

General Methods. All manipulations of air- and moisture-sensitive compounds were performed under a dry and oxygen-free nitrogen atmosphere by use of standard Schlenk techniques or under a nitrogen atmosphere in a Mbraun glovebox. Nitrogen (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-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 purified by use of a SPS-800 solvent purification system (Mbraun) and stored over fresh Na chips in the glovebox. Styrene was purchased from Kanto Chemical Co., Ltd., dried by stirring with CaH_2 for 24 h, vacuum-transferred, and degassed by two freeze−pump−thaw cycles. 1,5-Hexadiene (HD) was purchased from TCI, dried over Na chips and tripropylaluminum, vacuum-transferred, and degassed by two freeze−pump−thaw cycles. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Tosoh Finechem Corp. and used without purification. $Cp'Sc(CH_2SiMe_3)_2(THF)$ (**1a**: $Cp' = C_5H_5$; **1b**: $Cp' = C_5H_4Me$; **1c**: $Cp' = C_5HMe_4$; **1d**: $Cp' = C_5Me_5$; **1e**: $Cp' = C_5Me_4SiMe_3$), $(C_5Me_4R)Sc(CH_2SiMe_3)_2$ (**2**: $R = CH_2CH_2PPh_2$; **3**: $R = C_6H_4OMe\text{-}o$) and $Cp'Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**4c**: $Cp' = C_5HMe_4$; **4d**: $Cp' = C_5Me_5$; **4e**: $Cp' = C_5Me_4SiMe_3$) were synthesized as described previously.[11d,f] The deuterated solvents benzene-d_6 (99.5 atom % D) and 1,1,2,2-tetrachloroethane-d_2 (99.6 atom % D) were obtained from Cambridge Isotope.

The NMR data of the HD homopolymers, the styrene homopolymers, the HD−styrene copolymers, and the HD−styrene−ethylene terpolymers were obtained on a JEOL JNM-AL 300 or JNM-ECA 600 spectrometer in 1,1,2,2-tetrachloroethane-d_2 at room temperature (HD homopolymers and atactic polystyrenes), 80 °C (HD−styrene copolymers), or 100 °C (HD−styrene−ethylene terpolymers). All 2D NMR experiments were performed on a JEOL ECA 600 NMR spectrometer with a 5 mm gradient tunable broad-band double resonance JEOL FGTH5 probe, operating at 600.17 MHz for ^1H and 150.91 MHz for ^{13}C NMR. Heteronuclear 2D $^1H-^{13}C$ HSQC, H2BC, HMBC, and HSQC-TOCSY experiments were measured using standard NMR pulse sequence of Delta version 5.01, and typical data matrix sizes were 256 and 1K points and were zero-filled to 512 points or linear predicted to 1K in the F_1 domain prior to FT. The H2BC experiments were performed with the constant time delay of 22 ms and low-pass J filters in the range of 120−160 Hz. The HMBC experiments were measured using 50 or 62.5 ms of the duration time for long-range coupling. The editing HSQC-TOCSY experiments were measured using a mixing time of 5, 15, 30, or 45 ms. Typical conditions for ^{13}C NMR experiments were as follows: 45° pulse width, 4.57 μs; acquisition time, 0.72 s; sweep width, 45 290 Hz; relaxation delay, 0.89 s; number of acquisitions, 6400 ; data size, 32K; line broadening, 2.0 Hz.

The molecular weights and the molecular weight distributions of the HD homopolymers and the atactic polystyrenes were determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8220 GPC apparatus (Tosoh Corp.). THF was employed as an eluent at a flow rate of 0.35 mL/min. The calibration was made by polystyrene standard. The molecular weights and the molecular weight distributions of the syndiotactic polystyrenes, the HD−styrene copolymers, and the HD−styrene−ethylene terpolymers were determined at 145 °C by high-temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corp.). o-Dichlorobenzene was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard. The DSC measurements were performed on a DSC6220 (SII Co.) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 20 °C/min to −50 °C, and then recording the second DSC scan.

Preparation of $(C_5H_5)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (4a). In a glovebox, a THF solution (12 mL) of $Sc(CH_2C_6H_4NMe_2\text{-}o)_3$ (1.792 g, 4.000 mmol) was added to a THF solution (6 mL) of C_5H_6 (0.317 g, 4.800 mmol) in a Schlenk tube with a Teflon stopcock. This tube was taken outside and heated at 40 °C for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane. A concentrated hexane solution at −30 °C gave **4a** as yellow crystals (1.226 g, 81% yield). ^1H NMR (C_6D_6, 50 °C): 1.47 (s, 4H, CH_2), 2.32 (s, 12H, NMe_2), 5.79 (s, 5H, C_5H_5), 6.73−7.05 (m, 8H, aryl). ^{13}C NMR (C_6D_6, 25 °C): 44.5 (CH_2), 46.6 (NMe_2), 112.2, 117.2, 120.9, 127.2, 130.1, 144.0, 145.7 (aromatics and Cp ring carbons). Anal. Calcd for $C_{23}H_{29}ScN_2$: C 72.99; H 7.72; N 7.40. Found: C 73.44; H 7.75; N 7.45.

Preparation of $(C_5H_4Me)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (4b). In a glovebox, a THF solution (12 mL) of $Sc(CH_2C_6H_4NMe_2\text{-}o)_3$ (1.792 g, 4.000 mmol) was added to a THF solution (6 mL) of C_5H_5Me (0.317 g, 4.800 mmol) in a Schlenk tube with a Teflon stopcock. This tube was taken outside and heated at 40 °C for 2 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane. A concentrated hexane solution at −30 °C gave **4b** as yellow crystals (1.255 g, 80% yield). ^1H NMR (C_6D_6, 50 °C): 1.43 (s, 4H, CH_2), 2.08 (s, 3H, C_5H_4Me), 2.34 (s, 12H, NMe_2), 5.26 (s, 2H, C_5H_4Me), 5.82 (t, 2H, C_5H_4Me), 6.73−7.05 (m, 8H, aryl). ^{13}C NMR (C_6D_6, 25 °C): 14.9 (C_5H_4Me), 45.0 (CH_2), 46.8 (NMe_2), 112.2, 112.4, 117.2, 120.9, 124.1, 126.9, 130.1, 144.0, 146.0 (aromatics and Cp ring carbons). Anal. Calcd for $C_{24}H_{31}ScN_2$: C 73.45; H 7.96; N 7.14. Found: C 73.50; H 7.95; N 7.23.

A Typical Procedure for the Polymerization of HD (Table 1, Run 12). In a glovebox, 1,5-hexadiene (783 mg, 9.5 mmol) was added under vigorous stirring to a reaction mixture of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) in toluene (6 mL). The polymerization reaction was terminated by addition of methanol. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol and dried under vacuum at 60 °C to a constant weight. The VTM content of the HD homopolymer was calculated according to the following formula:

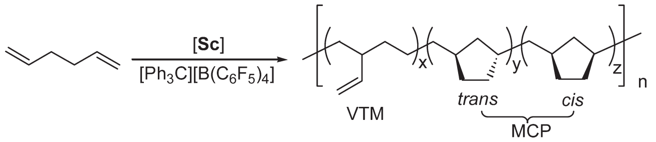
$$\text{VTM mol \%} = \{0.5I_1/[0.5I_1 + 0.1(I_2 - 3.5I_1)]\} \times 100$$

where I_1 is the integration of the resonance at 5.0 ppm (two vinyl protons of the VTM unit) and I_2 is the integration of the resonances from 0.7 to 2.0 ppm (seven aliphatic protons of the VTM unit and ten aliphatic protons of the MCP unit) in the ^1H NMR spectrum of the HD homopolymer.

A Typical Procedure for the Polymerization of Styrene (Table 2, Run 12). In a glovebox, styrene (1.30 g, 12.5 mmol) was added under vigorous stirring to a reaction mixture of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (13 mg, 25 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (23 mg, 25 μmol) in toluene (8 mL). The polymerization reaction was terminated by addition of methanol. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight.

A Typical Procedure for the Copolymerization of HD and Styrene (Table 3, Run 9). In a glovebox, a mixture of 1,5-hexadiene (390 mg, 4.75 mmol) and styrene (495 mg, 4.75 mmol) was added

Table 1. Homopolymerization of 1,5-Hexadiene by Half-Sandwich Scandium−Dialkyl Complexes[a]



					composition[c] (%)					
run	[Sc]	time (min)	yield (%)	activity[b]	MCP (*trans*/*cis*)	VTM	M_n[d] ($\times 10^3$)	M_w/M_n[d]	T_g[e] (°C)	T_m[e] (°C)
1	**1a**	180	89	12.2	93 (54/46)	7	4	3.77	−13	55
2	**1b**	180	72	9.9	92 (56/44)	8	6	3.95	−7	64
3	**1c**	80	91	28.1	cross-linked polymer		n.m.[f]	n.m.	n.m.	n.m.
4	**1d**	1	100	2471	cross-linked polymer		n.m.	n.m.	n.m.	n.m.
5	**1e**	1	100	2471	cross-linked polymer		n.m.	n.m.	n.m.	n.m.
6	**2**	10	23	56.8	cross-linked polymer		n.m.	n.m.	n.m.	n.m.
7	**3**	10	100	247	cross-linked polymer		n.m.	n.m.	n.m.	n.m.
8	**4a**	180	80	11.0	95 (50/50)	5	6	2.25	−18	69
9	**4b**	180	40	5.5	93 (54/46)	7	7	2.19	−8	69
10	**4c**	180	67	9.2	83 (67/33)	17	9	2.47	−12	
11	**4d**	180	88	12.1	85 (74/26)	15	16	2.88	−7	
12	**4e**	80	91	28.1	83 (86/14)	17	16	2.56	−7	
13	**4e**[g]	80	88	27.2	82 (85/15)	18	13	2.27	−12	
14	**4e**[h]	180	trace							

[a] Conditions: [Sc], 19 μmol; $[Ph_3C][B(C_6F_5)_4]$, 19 μmol; 1,5-hexadiene, 9.5 mmol; toluene, 6 mL; 25 °C; unless otherwise noted. [b] Given in kilograms of polymer/(mol Sc h). [c] Determined by ^{1}H NMR and ^{13}C NMR. [d] Determined by GPC in THF at 40 °C against polystyrene standard. [e] Determined by DSC. [f] n.m. = not measured. [g] $[PhMe_2NH][B(C_6F_5)_4]$, 19 μmol. [h] $B(C_6F_5)_3$, 19 μmol.

under vigorous stirring to a reaction mixture of $(C_5Me_4SiMe_3)Sc$ ((18 mg, 19 μmol) in toluene (6 mL). The polymerization reaction was terminated by addition of methanol after 30 min. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight. The styrene (St), VTM, and MCP contents of the HD−styrene copolymer were calculated according to the following formula:

$$\text{St mol \%} = \{0.2I_3/[0.2I_3 + 0.5I_1 + 0.1(I_2 - 3.5I_1 - 0.6I_3)]\} \times 100$$

$$\text{VTM mol \%} = \{0.5I_1/[0.2I_3 + 0.5I_1 + 0.1(I_2 - 3.5I_1 - 0.6I_3)]\} \times 100$$

$$\text{MCP mol \%} = 100 - \text{St mol \%} - \text{VTM mol \%}$$

where I_1 and I_2 are defined as above and I_3 is the integration of the resonances from 6.6 to 7.0 ppm (five phenyl protons of the styrene unit) in the ^{1}H NMR spectrum of the HD−styrene copolymer.

A Typical Procedure for the Terpolymerization of HD with Styrene and Ethylene (Table 4, Run 4). In the glovebox, a toluene solution (2 mL) of 1,5-hexadiene (390 mg, 4.75 mmol) and styrene (495 mg, 4.75 mmol) was charged into a two-necked flask with a magnetic stir 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 stopcock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A toluene solution (4 mL) of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) was then added through a syringe under vigorous stirring. The polymerization reaction was quenched after 2 min by addition of methanol. The polymer product was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight. The styrene (St), VTM, and MCP contents of the HD−styrene−ethylene terpolymer were calculated according to the following formulas:

$$\text{St mol \%} = \{0.2I_3/[0.2I_3 + 0.5I_1 + (1 + I_4/I_5)(I_6 - 3.5I_1 - 0.6I_3)/(10 + 4I_4/I_5)]\} \times 100$$

$$\text{VTM mol \%} = \{0.5I_1/[0.2I_3 + 0.5I_1 + (1 + I_4/I_5)(I_6 - 3.5I_1 - 0.6I_3)/(10 + 4I_4/I_5)]\} \times 100$$

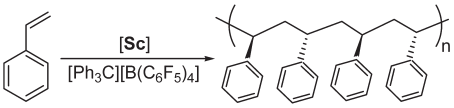
$$\text{MCP mol \%} = \{[(I_6 - 3.5I_1 - 0.6I_3)/(10 + 4I_4/I_5)]/[0.2I_3 + 0.5I_1 + (1 + I_4/I_5)(I_6 - 3.5I_1 - 0.6I_3)/(10 + 4I_4/I_5)]\} \times 100$$

$$\text{Et mol \%} = 100 - \text{St mol \%} - \text{VTM mol \%} - \text{MCP mol \%}$$

where I_1 and I_3 are defined as above, I_4 is the integration of the resonances from 25.9 to 30.4 ppm (two methylene carbons of the ethylene unit), and I_5 is the integration of the resonances from 31.6 to 33.2 ppm (two methylene carbons of the MCP unit) in the ^{13}C NMR spectrum of the HD−styrene−ethylene terpolymer; I_6 is the integration of the resonances from 0.7 to 2.0 ppm (seven aliphatic protons of the VTM unit, ten aliphatic protons of the MCP unit, three aliphatic protons of styrene unit and four methylene protons of the ethylene unit) in the ^{1}H NMR spectrum of the HD−styrene−ethylene terpolymer.

A Typical Procedure for the Hydroxylation of the HD−Styrene Copolymer. Into a Schlenk tube under a nitrogen atmosphere, the HD−styrene copolymer (311 mg, from Table 3, run 9), 9-borobicyclo[3.3.1]nonane (277 mg, 2 equiv to the olefinic double bonds), toluene (20 mL), and THF (20 mL) were added. The mixture

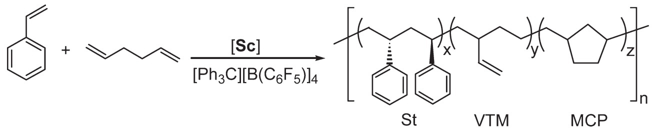
Table 2. Homopolymerization of Styrene by Half-Sandwich Scandium−Dialkyl Complexes[a]



run	[Sc]	time (min)	yield[b] (%)	activity[c]	M_n (×10^3)[d]	M_w/M_n[d]	T_g[e] (°C)	T_m[e] (°C)
1	**1a**	240	9[f]	1.1	7	2.08	94	
2	**1b**	240	20[f]	2.6	13	1.76	92	
3	**1c**	120	92	24	97	1.57		269
4	**1d**	1	96	3000	89	1.29		271
5	**1e**	1	100	3125	98	1.25		274
6	**2**	60	trace					
7	**3**	1	100	3125	98	1.25		274
8	**4a**	35	73[f]	65	41	2.10	95	
9	**4b**	35	94[g]	84	46	2.04		230
10	**4c**	25	95	119	68	2.46		271
11	**4d**	1	100	3125	243	1.69		271
12	**4e**	1	100	3125	252	1.53		271

[a] Conditions: [Sc], 25 μmol; [Ph_3C][$B(C_6F_5)_4$], 25 μmol; styrene, 12.5 mmol; toluene, 8 mL; 25 °C. [b] Yield of syndiotactic polystyrene (*rrrr* > 99%), unless otherwise noted. [c] Given in kilograms of polymer/(mol Sc h). [d] Determined by GPC in *o*-dichlorobenzene at 145 °C against polystyrene standard. [e] Determined by DSC. [f] Atactic polystyrene. [g] Syndiotactic polystyrene (*rrrr* = 70%).

Table 3. Copolymerization of 1,5-Hexadiene (HD) with Styrene (St) by Half-Sandwich Dialkyl−Scandium Complexes[a]



run	[Sc]	St[b]	HD[b]	yield (g)	activity[c]	composition (mol %)[d] St	composition (mol %)[d] MCP	composition (mol %)[d] VTM	M_n[e] (×10^3)	M_w/M_n[e]	T_g[f] (°C)	T_m[f] (°C)
1	**1e**	250	250	0.195	20.5	100[g]	0	0	15	1.70	n.m.[j]	n.m.
2	**3**	250	250	0.289	30.4	100[g]	0	0	21	1.72	n.m.	n.m.
3	**4a**	250	250	0.177	18.6	100[h]	0	0	14	2.02	n.m.	n.m.
4	**4a**	150	350	0.156	16.4	76	23	1	12	1.99	65	
5	**4b**	250	250	0.185	19.5	100[h]	0	0	16	1.98	n.m.	n.m.
6	**4b**	150	350	0.107	11.3	83	16	1	11	1.79	71	
7	**4c**	250	250	0.445	46.8	92	5	3	33	2.70	82	224
8	**4d**	250	250	0.472	49.7	88	9	3	54	2.80	79	229
9	**4e**	250	250	0.562	59.2	74	22	4	41	2.29		256
10	**4e**	10	490	0.351	36.9	14	72	14	17	2.47	−3	
11	**4e**	50	450	0.234	24.6	32	56	12	13	2.48	−1	
12	**4e**	100	400	0.498	52.4	35	53	12	24	2.57	−1	225
13	**4e**	150	350	0.369	38.8	57	37	6	31	2.44		242
14	**4e**	200	300	0.583	61.4	63	32	5	45	2.37		253
15	**4e**	275	225	0.565	59.5	86	11	3	55	2.71		260
16[i]	**4e**	500	750	1.482	156.0	64	31	5	84	2.47		251

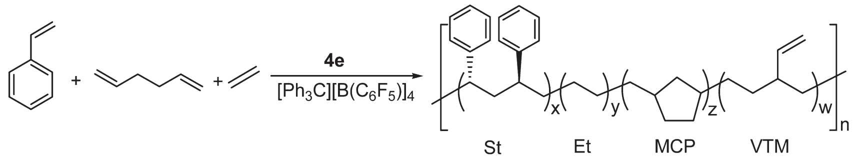
[a] Conditions: [Sc], 19 μmol; [Ph_3C][$B(C_6F_5)_4$], 19 μmol; toluene, 6 mL; reaction time, 30 min; 25 °C; unless otherwise noted. [b] Molar ratio to [Sc]. [c] Given in kilograms of polymer/(mol Sc h). [d] Determined by ^{1}H NMR. [e] Determined by GPC in *o*-dichlorobenzene at 145 °C against polystyrene standard. [f] Determined by DSC. [g] Syndiotactic polystyrene. [h] Atactic polystyrene. [i] Toluene, 15 mL. [j] n.m. = not measured.

was stirred at 65 °C for 3 h. The resulting mixture was then added to NaOH (18 mg) and a 30% H_2O_2 aqueous solution (75 mg) and stirred for an additional 3 h at 40 °C. The mixture was then poured into methanol; the resultant polymer was collected on a filter paper by filtration, adequately washed with methanol, and dried under vacuum at 60 °C to a constant weight.

■ RESULTS AND DISCUSSION

Homopolymerization of 1,5-Hexadiene (HD). The homopolymerization of HD was first examined by use of the scandium−dialkyl complexes bearing various Cp′ ligands (Chart 1) in combination with [Ph_3C][$B(C_6F_5)_4$] as a cocatalyst. Some

Table 4. Terpolymerization of 1,5-Hexadiene (HD) with Styrene (St) and Ethylene (Et) by 4e[a]



run	St[b]	HD[b]	yield (g)	activity[c]	composition (mol %)[d] St	Et	MCP	VTM	M_n[e] ($\times 10^3$)	M_w/M_n[e]	T_m[f] (°C)
1	100	400	0.668	1054	7	66	26	1	110	1.28	120
2	150	350	0.586	925	16	62	21	1	90	1.45	119, 206
3	200	300	0.779	1230	20	58	21	1	110	1.40	101, 224
4	250	250	0.747	1179	32	50	17	1	110	1.53	100, 230
5	300	200	0.857	1353	38	49	12	1	115	1.49	109, 243
6[g]	300	700	1.342	2119	23	56	20	1	128	1.37	108, 228

[a] Conditions: [Sc], 19 μmol; [Ph$_3$C][B(C$_6$F$_5$)$_4$], 19 μmol; P_{ethylene}, 1 atm; toluene, 6 mL; reaction time, 2 min; 25 °C; unless otherwise noted. [b] Molar ratio to [Sc]. [c] Given in kilograms of polymer/(mol Sc atm h). [d] Determined by ^{1}H NMR and ^{13}C NMR. [e] Determined by GPC in *o*-dichlorobenzene at 145 °C against polystyrene standard. [f] Determined by DSC. [g] Toluene, 12 mL.

representative results are summarized in Table 1. Significant ligand influence on the activity and selectivity of the polymerization was observed. The THF-containing, trimethylsilylmethyl (Me$_3$SiCH$_2$) complexes bearing relatively small C$_5$H$_5$ (**1a**) and C$_5$H$_4$Me (**1b**) ligands effectively catalyzed the HD cyclopolymerization to give soluble poly(HD) with predominant methylene-1,3-cyclopentane (MCP) units (92−93%) and a small amount of vinyltetramethylene (VTM) units (7−8%) (Table 1, runs 1 and 2). However, the analogous Sc complexes with larger Cp′ ligands such as C$_5$HMe$_4$ (**1c**), C$_5$Me$_5$ (**1d**), and C$_5$Me$_4$SiMe$_3$ (**1e**) yielded insoluble cross-linked polymer materials under the same conditions (Table 1, runs 3−5). Similarly, the half-sandwich Sc complexes **2** and **3**, which bear the Cp′ ligands with a heteroatom-containing side arm, also led to formation of insoluble cross-linked polymers (Table 1, runs 6 and 7). In sharp contrast, the THF-free, aminobenzyl half-sandwich scandium complexes **4a**−**4e** all gave well-defined cyclopolymers, irrespective of the steric hindrance of the Cp′ ligands (Table 1, runs 8−12). The VTM content of the resulting polymers increased from 5% to 17%, when the steric hindrance of the Cp′ ligands was decreased from C$_5$H$_5$ (**4a**) to C$_5$Me$_4$SiMe$_3$ (**4e**). The *trans* configuration in the MCP units increased from 50% to 86%, as the steric hindrance of the Cp′ ligands became larger. These results suggest that it is possible to tune the microstructure of the polymers by modifying the Cp′ ligands. The trityl and anilinium borates [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [PhMe$_2$NH][B(C$_6$F$_5$)$_4$] showed similar influences on the polymerization activity and selectivity, while the neutral borane compound B(C$_6$F$_5$)$_3$ showed almost no activity for the homopolymerization of HD (Table 1, runs 12−14).

Homopolymerization of Styrene. The homopolymerization of styrene by the half-sandwich scandium−dialkyl complexes was examined in toluene at room temperature. Some representative results are summarized in Table 2. Significant influence of the Cp′ ligands on the polymerization of styrene was also observed, but the influence of the THF ligand was not as critical as in the case of HD polymerization. The Sc complexes bearing the small C$_5$H$_5$ (**1a** and **4a**) and C$_5$H$_4$Me (**1b** and **4b**) ligands were active for the polymerization of styrene but gave atactic polystyrene (Table 2, runs 1, 2, 8, and 9). In contrast, the analogous complexes with larger Cp′ ligands such as C$_5$HMe$_4$ (**1c** and **4c**), C$_5$Me$_5$ (**1d** and **4d**), and C$_5$Me$_4$SiMe$_3$ (**1e** and **4e**) all afforded selectively syndiotactic polystyrene (Table 2, runs 4, 5, 11, and 12).[11a] Among these complexes, the most sterically demanding ligand C$_5$Me$_4$SiMe$_3$ (**1e** and **4e**) gave the highest activity. Unexpectedly to us, the Sc complex with a diphenylphosphine-containing Cp ligand (**2**) showed almost no activity for the polymerization of styrene (Table 2, run 6), while the analogous methoxy-containing Cp-ligated complex **3** was highly active for the syndiospecific polymerization of styrene under the same conditions (Table 2, run 7).

Copolymerization of 1,5-Hexadiene (HD) with Styrene. On the basis of the experimental results of the homopolymerization of HD and styrene, the THF-free aminobenzyl complexes **4a**−**4e** were chosen to examine the copolymerization of HD and styrene. Some representative results are summarized in Table 3. Complexes **4a** and **4b**, which bear the relatively small C$_5$H$_5$ and C$_5$H$_4$Me ligands, respectively, did not give a copolymer product but yielded atactic homopolystyrene in the presence of 250 equiv of HD and styrene (Table 3, runs 3 and 5). When the HD/styrene feed ratio was increased from 250/250 to 350/150, the copolymerization took place to give HD−styrene copolymers containing atactic styrene−styrene sequences (76−83 mol %) and MCP units (16−23 mol %) together with a small amount of VTM units (1 mol %) (Table 3, runs 4 and 6). In striking contrast, the analogous Sc complexes with lager C$_5$HMe$_4$ (**4c**), C$_5$Me$_5$ (**4d**), and C$_5$Me$_4$SiMe$_3$ (**4e**) ligands afforded the HD−styrene copolymers containing syndiotactic styrene−styrene sequences (74−92 mol %) together with MCP (5−22 mol %) and VTM (3−4 mol %) units in the presence of 250 equiv of HD and styrene (Table 3, runs 7−9). The HD content (MCP + VTM) in the resulting copolymers decreased (or the styrene content increased) as the steric hindrance of the Cp′ ligands increased in **4c**−**4e**. Solvent fractionation experiments confirmed that the resulting polymer products are true HD−styrene copolymers, which do not contain homopolymers.[14] For comparison, the C$_5$Me$_4$SiMe$_3$-ligated, THF-containing (trimethylsilyl)methyl complex **1e** and the methoxy-containing half-sandwich complex **3** were also examined for the copolymerization of HD and styrene, which, however, did not give a copolymer product

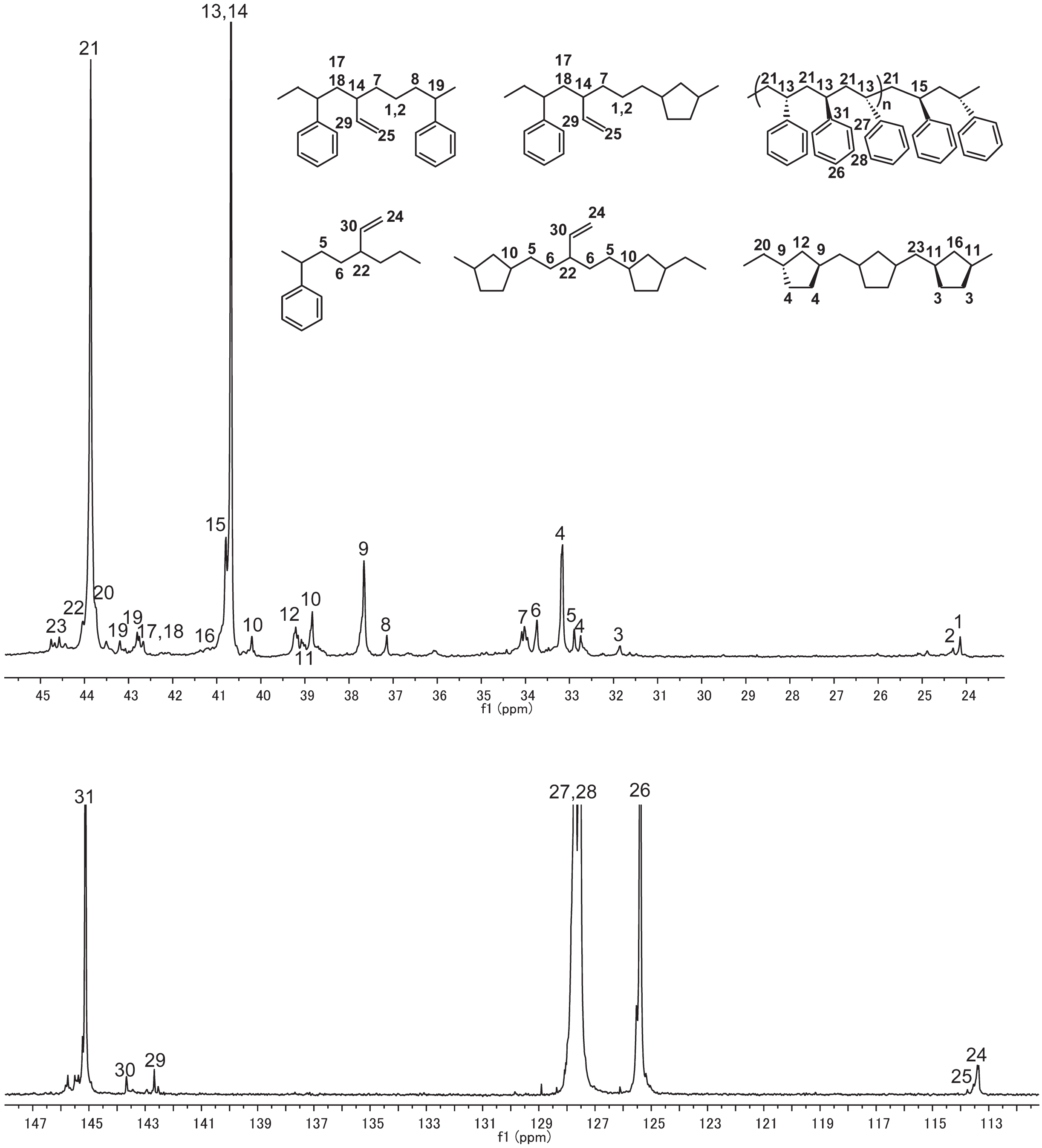


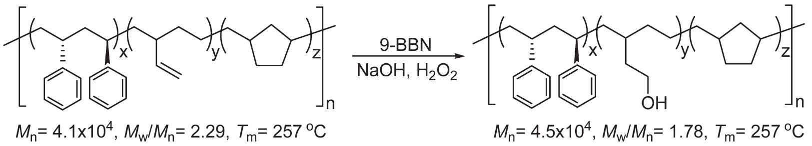
Figure 1. ^{13}C NMR (150.9 MHz) spectrum of a 1,5-hexadiene−styrene copolymer (Table 3, run 9) in 1,1,2,2-tetrachloroethane-d_2 at 80 °C.

but yielded only syndiotactic homopolystyrene in the presence of 250 equiv of HD and styrene (Table 3, runs 1 and 2), demonstrating again that the coordination of a Lewis base ligand such as THF to the metal center can show significant influence on the activity and selectivity of the polymerization reaction.

The THF-free, aminobenzyl complex **4e** with the C_5Me_4-$SiMe_3$ ligand was then utilized to examine the HD−styrene copolymerization with different HD/styrene feeding ratios (Table 3, runs 9−16). As the HD/styrene feed ratio was raised, the HD content in resulting copolymers increased significantly. A new family of polymer materials with styrene content = 14−86 mol %, MCP content = 11−72 mol %, and VTM content = 3−14 mol % were thus obtained simply by changing the HD/styrene feed ratio. It is also noteworthy that the increase of the feeding amount of both HD and styrene (or monomer/catalyst ratio) led to significant increase of the catalytic activity (yield) as well as increase of the molecular weight of the copolymer product (Table 3, run 16).

The GPC curves of all the HD−styrene copolymers are unimodal with moderate molecular weight distribution (M_w/M_n = 2.29−2.71), indicating the predominance of a single-site active catalyst species. The melting temperatures (T_m) of the copolymers prepared by **4e** with styrene content = 35−86 mol % varied in the range of 226−260 °C, which are lower than that (ca. 270 °C) of pure syndiotactic polystyrene, and increased with increasing styrene content (Table 3, runs

Scheme 1. Hydroxylation of HD−Styrene Copolymers



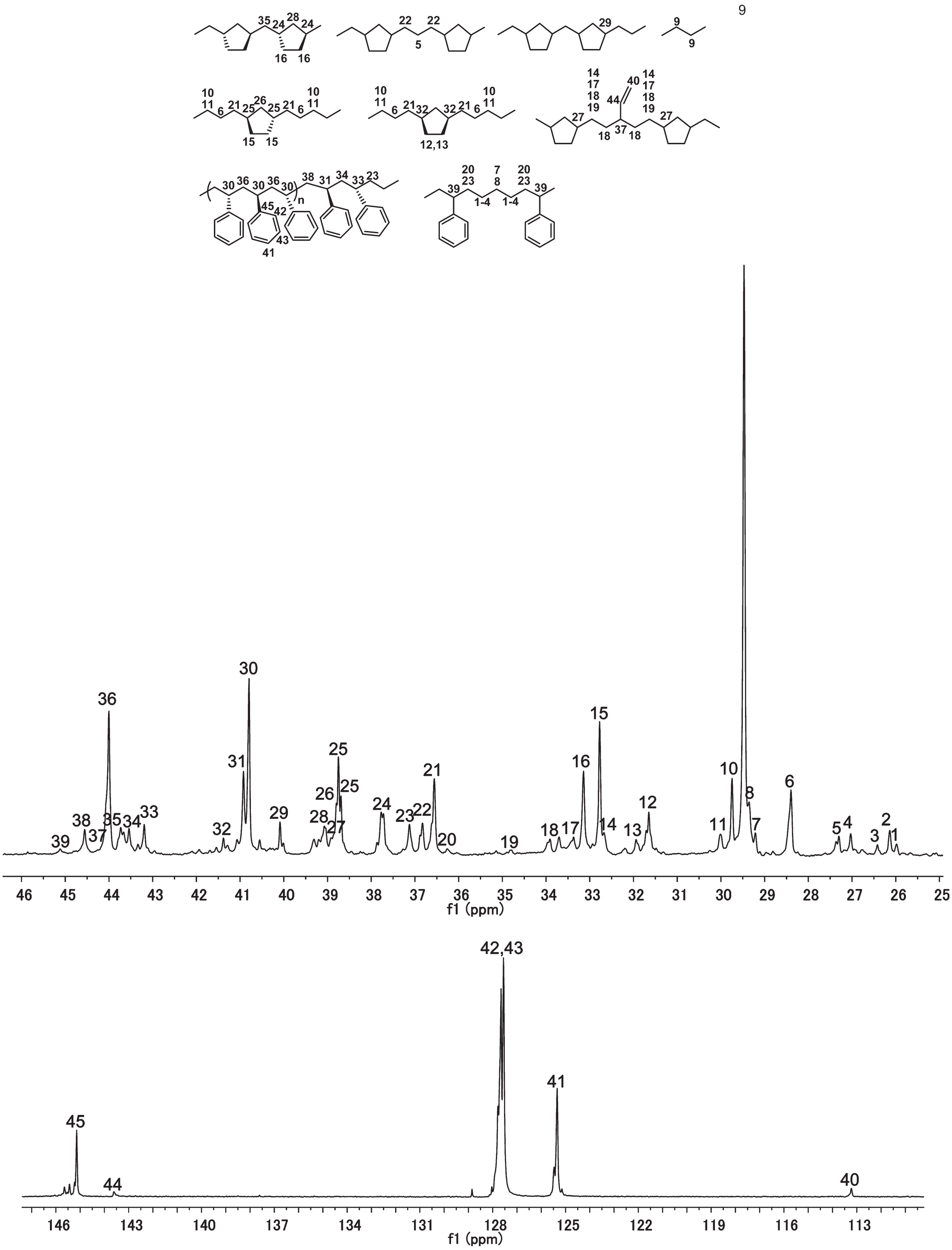
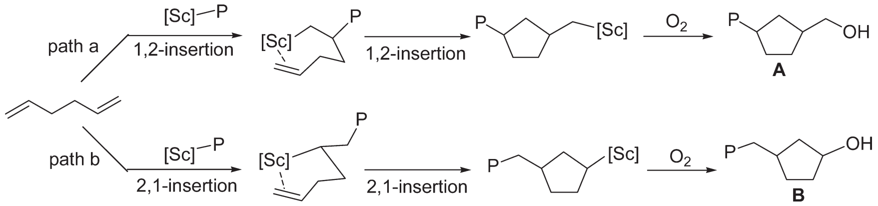


Figure 2. ^{13}C NMR (150.9 MHz) spectrum of a 1,5-hexadiene−styrene−ethylene terpolymer (Table 4, run 3) in 1,1,2,2-tetrachloroethane-d_2 at 100 °C.

Scheme 2. Possible Pathways for the Formation of the MCP Units



12−16). When the styrene content was below 32 mol %, a melting point was not observed.

The Fineman−Ross plots of the copolymerization at very low monomer conversion (<5%) in the presence of **4e**/[Ph_3C][$B(C_6F_5)_4$] gave the monomer reactivity ratios $\gamma_{St} = k_{StSt}/k_{StHD}$ = 23.7 and $\gamma_{HD} = k_{HDHD}/k_{HDSt}$ = 0.02, which suggest that the formation of styrene−styrene sequences (blocks) is preferred in the present HD−styrene copolymerization. The present efficient copolymerization of HD and styrene by **4e** is in sharp contrast with what was observed in previous attempts to copolymerize 1,6-heptadiene (HPD) with styrene, which did not give a copolymer but yielded a mixture of homopolymers.[11i]

The microstructures of the HD−styrene copolymers were characterized by detailed NMR spectral data analyses (see Supporting Information). Methine and methylene carbons were distinguished by the DEPT spectrum. Direct ^{1}H−^{13}C correlations were established by HSQC spectral data. Stereochemistry of syndiotactic styrene−styrene blocks and *trans*-MCP−MCP blocks were confirmed by the HSQC cross-peak patterns of the methylenes with equivalent hydrogen. Correlations around methine carbons were assigned by the H2BC[15] (heteronuclear two-bond correlation) and HMBC (heteronuclear multiple-bond correlation) analyses. HMBC cross-peaks from aromatic and olefinic protons were used to assign styrene and VTM units. Editing HSQC-TOCSY spectra with several mixing times were also used for confirmation of assignments. Relatively weak signals were carefully assigned by comparison of spectral data with those of HD−stryrene copolymers having different monomer contents and those of related polymers reported previously. The ^{13}C NMR spectrum of a copolymer with styrene content of 74 mol % (Table 3, run 9) is shown in Figure 1. It was revealed that the HD−styrene copolymers are multiblock copolymers containing syndiotactic styrene−styrene blocks, MCP−MCP blocks, MCP−VTM sequences, and styrene−VTM sequences. Styrene−MCP sequences are negligible, probably owing to steric hindrance of the two sterically demanding units. The presence of styrene−VTM sequences and lack of styrene−MCP sequences in the present copolymer products could account for the observation that efficient HD−styrene copolymerization is possible, but the copolymerization of HPD with styrene is difficult.[11i]

Hydroxylation of the VTM units in the HD−styrene copolymers could be easily achieved by hydroboration followed by H_2O_2 oxidation, which quantitatively converted the vinyl groups into hydroxy groups (Scheme 1). No significant change in M_n, M_w/M_n, and T_m was observed between the VTM-containing starting material and the hydroxylated product. However, the hydroxylated polymers showed higher solubility in THF.

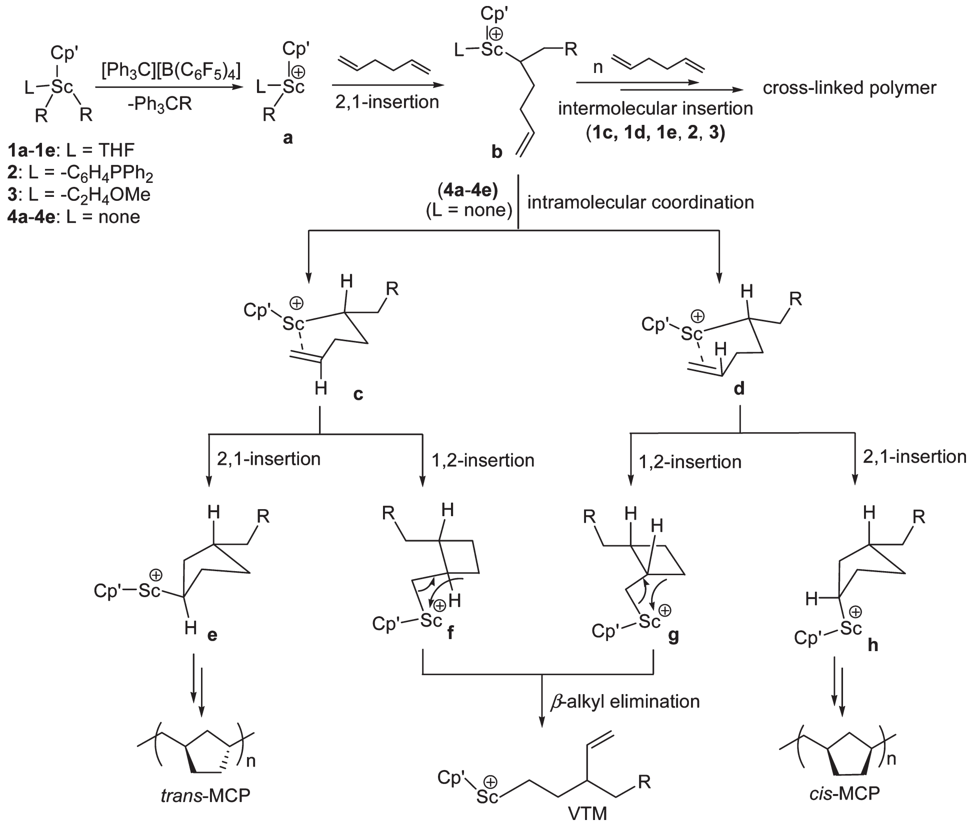
Terpolymerization of 1,5-Hexadiene (HD) with Styrene and Ethylene. The terpolymerization of HD with styrene and ethylene was carried out by use of **4e**/[Ph_3C][$B(C_6F_5)_4$] as a catalyst under 1 atm of ethylene with different HD/styrene feed ratios in toluene at 25 °C, which took place rapidly to give the HD−styrene−ethylene terpolymers with high molecular weight (M_n = 90−128 × 10^3) and narrow molecular weight distributions (M_w/M_n = 1.28−1.53) (Table 4). The terpolymer materials with styrene content = 7−38 mol %, ethylene content = 49−66 mol %, and MCP content = 12−26 mol % could be easily obtained simply by changing the HD/styrene feed ratio under 1 atm of ethylene. The VTM content in the resulting HD−styrene−ethylene terpolymers was ca. 1 mol % or less in all the cases, in contrast with what was observed in the HD homopolymerization or the HD−styrene copolymerization (see Tables 1 and 3). The increase of the feeding amount of both HD and styrene under 1 atm of ethylene led to significant increase of the catalytic activity (or polymer yield) and the molecular weight of the terpolymer product (Table 4, run 6), similar what was observed in the HD−styrene copolymerization. Most of the HD−styrene−ethylene terpolymers obtained above showed two melting points at 100−119 and 206−241 °C which possibly originate from polyethylene blocks and syndiotactic polystyrene blocks, respectively (Table 4, runs 2−6).

The HD−styrene−ethylene terpolymers were also characterized by the ^{1}H, ^{13}C, DEPT, HSQC, H2BC, and HMBC NMR analyses (see Supporting Information), together with careful comparison of spectral data with those of HD−styrene copolymers. The ^{13}C NMR spectrum of a HD−styrene−ethylene terpolymer with styrene content = 20 mol %, ethylene content = 58 mol %, and HD content = 22 mol % (Table 4, run 3) is shown in Figure 2. It was revealed that these terpolymer products are multiblock copolymers, which mainly contain relatively long ethylene−ethylene blocks, syndiotactic styrene−styrene blocks, MCP−MCP blocks, MCP−ethylene sequences, and ethylene−styrene sequences, together with a small amount of MCP−VTM sequences. Similar to the HD−styrene copolymers, styrene−MCP sequences were not observed.

Polymerization Mechanism. In the cyclopolymerization of HD, there are two possible pathways for the formation of the MCP units, namely, primary (1,2-) insertion/cyclization and secondary (2,1-) insertion/cyclization (Scheme 2).[3e,4a−4d,16] To validate the MCP formation mechanism in the present polymerization system, a polymerization reaction in a low monomer/catalyst ratio ([HD]/[Sc] = 5) was quenched with O_2, and the end group of the resulting oligomer products was analyzed by ^{1}H NMR. A clear multiplet was observed at 4.3 ppm, which suggests the formation of a secondary alcohol such as **B** (Scheme 2).[17] No signals assignable to a primary alcohol like **A** were observed.[18] These results support the 2,1-insertion mechanism (Scheme 2, path b).[3e,16]

A possible mechanism of the polymerization of HD catalyzed by the present half-sandwich scandium complexes is shown in Scheme 3. The reaction of a half-sandwich scandium−dialkyl complex with [Ph_3C][$B(C_6F_5)_4$] would give a cationic scandium alkyl species such as **a**.[11d,f] The coordination of one C=C double bond of HD to the metal center and its subsequent insertion into

Scheme 3. A Possible Mechanism of Scandium-Catalyzed Polymerization of 1,5-Hexadiene (HD)



the Sc—R bond in a 2,1-fashion should give **b**. In the case of the THF-free scandium complexes **4a**—**4e** (or the THF-containing complexes bearing smaller Cp′ ligands **1a** and **1b**), intramolecular coordination of the remaining C═C double bond of the HD unit in **b** to the metal center would take place easily to afford **c** and/or **d**. The subsequent intramolecular insertion (cyclization) of the coordinated C═C double bond in a 2,1-fashion in **c** or **d** would yield the *trans*- or *cis*-MCP units through the intermediate **e** or **h**, respectively. If the insertion (cyclization) of the C═C double bond in **c** or **d** occurs in a 1,2-fashion, a four-member ring intermediate such as **f** or **g** would be formed, which could then give a VTM unit through an internal *β*-alkyl elimination to release the ring strain.[3e,19]

In the case of complexes **1c**, **1d**, **1e**, **2**, and **3**, which bear the sterically demanding Cp′ ligands together with a heteroatom (O or P) Lewis base unit bonding to the metal center, the intramolecular coordination of the C═C double bond in **b** would be hampered, and therefore the intermolecular coordination/insertion of the two C═C double bonds of HD would take place easier to yield cross-linked polymers.

In the copolymerization of HD with styrene or the terpolymerization of HD with styrene and ethylene, the coordination and insertion of a styrene molecule to the Sc—C bond in the VTM unit would be much easier than that in the MCP intermediates **e** and **h** because of steric hindrance in **e** and **h**. However, the coordination and insertion of ethylene into the Sc—C bond in both the VTM unit and the MCP intermediates **e** and **h** would be possible because ethylene is smaller than styrene. This scenario is in agreement with the experimental observations in the polymerization reactions.

■ CONCLUSION

We have demonstrated that half-sandwich scandium—dialkyl complexes in combination with an equivalent of $[Ph_3C][B(C_6F_5)_4]$ can serve as excellent catalysts for the polymerization and copolymerization of HD, styrene, and ethylene. The activity and selectivity of these catalysts are significantly influenced by the ligand environment around the metal center. The homopolymerization of HD by the THF-coordinated scandium (trimethylsilyl)methyl complexes with relatively small Cp′ ligands, such as **1a** and **1b**, affords soluble cyclopolymers containing predominant MCP units (up to 93%) and a small portion of VTM units. However, the more sterically demanding analogues such as **1c**, **1d**, **1e**, **2**, and **3** led to formation of insoluble cross-linked polymer products because of the steric hindrance and coordination of a Lewis base unit to the metal center, which may hamper the intramolecular coordination/insertion of the second C═C double of the HD unit. In contrast, the THF-free scandium aminobenzyl complexes **4c**—**4e** all give soluble cyclopolymers irrespective of difference in the steric bulk of the Cp′ ligands. By use of the $C_5Me_4SiMe_3$-ligated, THF-free aminobenzyl scandium complex **4e**, the copolymerization of HD and styrene has been achieved for the first time to give a series of cyclopolymer materials containing five-member ring MCP units and vinyl branch VTM units together with unique syndiotactic styrene—styrene sequences. More remarkably, the terpolymerization of HD, styrene, and ethylene has also been realized by use of this catalyst, yielding a new family of cyclopolymer materials containing five-member ring MCP units, ethylene—ethylene blocks, and syndiotactic styrene—styrene sequences, which show high melting points originating from both polyethylene blocks and syndiotactic polystyrene blocks. These results together with those reported previously[10,11] demonstrate again that the cationic half-sandwich scandium−alkyl complexes can serve as unique catalysts for the copolymerization of various olefins.

■ ASSOCIATED CONTENT

S Supporting Information. GPC curve, NMR spectra, and DSC charts of representative polymer products. This material is available free of charge via the Internet at http://pubs.acs.org.

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