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Cycloterpolymerization of 1,6-Heptadiene with Ethylene and Styrene Catalyzed by a THF-Free Half-Sandwich Scandium Complex

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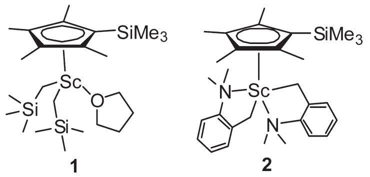
Supporting Information

The cycloterpolymerization of a nonconjugated diene such as 1,6-heptadiene (HPD) with ethylene and styrene is of much interest because it may afford a novel family of polymer materials that contain both five- and six-member ring cyclic structures together with aromatic units and therefore may show unique mechanical and optical properties.[1] However, no catalyst has been reported to date to effect such terpolymerization reactions. Previously, a few transition metal catalysts were reported for the homopolymerization of HPD.[2−6] However, attempts to copolymerize HPD with another monomer such as ethylene often gave a mixture of homopolymers.[7] A cobalt catalyst was reported recently by Osakada and co-workers to effect the copolymerization of HPD with ethylene to give HPD−ethylene copolymers with relatively low molecular weights.[7] The incorporation of styrene into a HPD-based polymer has not been reported previously, as far as we are aware. The use of rare-earth-based catalysts for the polymerization or copolymerization of HPD has been scarcely explored.[8]

We report here the polymerization and copolymerization of HPD with ethylene and styrene catalyzed by the half-sandwich scandium alkyl complexes. We found that whether or not the metal center bears a THF ligand can significantly influence the activity or selectivity. By using a THF-free aminobenzyl scandium complex, the cycloterpolymerization of HPD with ethylene and styrene has been achieved for the first time to give a new family of cyclopolyolefins containing both five- and six-member rings together with unique syndiotactic styrene−styrene sequences.[9]

At first, we examined the homopolymerization of HPD by use of the THF-containing half-sandwich scandium bis(trimethylsilylmethyl) complex [($C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$(THF)] (**1**) (Chart 1), which had previously shown excellent activity for the polymerization and copolymerization of ethylene, styrene, and other olefins.[10,11] The cyclopolymerization of HPD took place rapidly at room temperature in the presence of **1**/[Ph_3C][$B(C_6F_5)_4$] to give a cyclopolymer containing both six-member ring methylene-1,3-cyclohexane (MCH) units (86%) and five-member ring ethylene-1,2-cyclopentane (ECP) units (14%) (Table 1, run 1). However, the molecular weight of the polymer product is very low (M_n = 8 × 10^3) and the molecular weight distribution is rather broad (M_w/M_n = 5.61). A significant amount of 3-methylenecyclohexane end-groups were observed in the ^{1}H NMR spectrum (4.62 ppm), suggesting that β-H elimination may take place as a chain-termination reaction (vide infra). Because **1** contains a THF Lewis base ligand which might hamper the coordination and insertion of a C═C double bond at the metal center and thus jeopardize the chain propagation process, we then turned to examine the THF-free aminobenzyl complex [($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$] (**2**)[12] (Chart 1). To our delight, the THF-free complex **2** afforded poly(HPD) with a much higher molecular weight (M_n = 5.1 × 10^4) and narrower molecular weight distribution (M_w/M_n = 2.02) under the same conditions (Table 1, run 2). The resulting polymer product contains both six-member ring MCH units (91%) and five-member ring ECP units (9%), with the former being predominant over the latter.

Chart 1. Half-Sandwich Scandium Dialkyl Complexes with and without a THF Ligand



The copolymerization of HPD with ethylene (1 atm) by the THF-containing complex **1** at room temperature yielded the copolymer products showing a bimodal GPC profile, together with a significant amount of insoluble polymer materials, which might result from possible cross-linking reactions (Table 1, run 3). In contrast, the THF-free complex **2** afforded selectively a soluble HPD−ethylene copolymer showing a well-defined unimodal GPC profile under the same reaction conditions (Table 1, run 4). Complex **2** was then used to further examine the copolymerization of HPD. When the molar ratio of HPD to **2** was raised from 300 to 500 under 1 atm of ethylene, the HPD content of the resulting copolymers increased from 44 to 63 mol % (Table 1, runs 4 and 5). When styrene was introduced into the HPD−ethylene copolymerization system, the terpolymerization of HPD, ethylene, and styrene took place rapidly to give exclusively the corresponding terpolymers. The HPD content (8−52 mol %) and styrene content (15−83 mol %) in the terpolymers could be easily controlled simply by changing the HPD/styrene feed ratio under 1 atm of ethylene (Table 1, runs 7−10). In the absence of ethylene, the copolymerization of HPD

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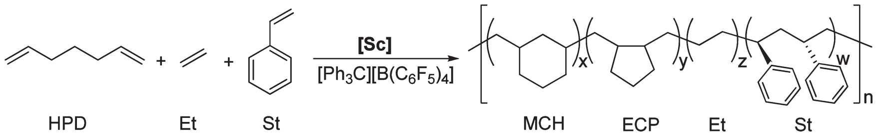
Table 1. Scandium-Catalyzed Terpolymerization of 1,6-Heptadiene (HPD) with Ethylene (Et) and Styrene (St)[a]



run	[Sc]	HPD[b]	St[b]	p_{ethylene} (atm)	time (min)	yield(g)	activity[c]	composition[d] (mol %) MCH	ECP	St	Et	M_n[e] (×10^4)	M_w/M_n[e]	T_g[f] (°C)	T_m[f] (°C)
1[g]	**1**	500	0	0	20	0.877	138	86	14	0	0	0.8[h]	5.61[h]	57	
2[g]	**2**	500	0	0	20	0.780	123	91	9	0	0	5.1[h]	2.02[h]	80	
3	**1**	300	0	1	3	0.519[i]	546	53	10	0	37	0.6; 32.9	4.06; 1.72	57	109
4	**2**	300	0	1	3	0.492	517	31	13	0	53	2.1[h]	2.49[h]	39	
5	**2**	500	0	1	3	0.520	547	46	17	0	37	2.0[h]	2.79[h]	41	
6[g]	**2**	300	200	0	20	0.847[j]						n.d.[k]	n.d.[k]	n.d.[k]	n.d.[k]
7	**2**	100	400	1	2	0.868	1370	8	0	83	9	6.6	2.22		266
8	**2**	200	300	1	2	0.824	1301	17	6	49	28	5.4	2.42		263
9	**2**	300	200	1	2	0.584	922	24	8	48	20	4.5	2.13		262
10	**2**	400	100	1	2	0.753	1189	39	13	15	33	3.8	2.03		247
11[l]	**2**	1200	800	1	2	2.342	3698	22	7	53	18	15.0	1.65		258

[a] Conditions: [Sc], 19 μmol; $[Ph_3C][B(C_6F_5)_4]$, 19 μmol; chlorobenzene, 2 mL; 25 °C; unless otherwise noted. [b] Molar ratio to [Sc]. [c] Given in kilograms of copolymer/(mol Sc h atm). [d] Determined by ^{13}C NMR. [e] Determined by GPC in *o*-dichlorobenzene at 145 °C against polystyrene standard, unless otherwise noted. [f] Determined by DSC. [g] Chlorobenzene, 6 mL. [h] Determined by GPC in THF at 40 °C against polystyrene standard. [i] Insoluble part, 0.102 g. [j] A mixture of poly(HPD) and syndiotactic polystyrene. Homopoly(HPD) was soluble, but syndiotactic polystyrene was insoluble in THF. [k] n.d. = not determined. [l] Chlorobenzene, 8 mL.

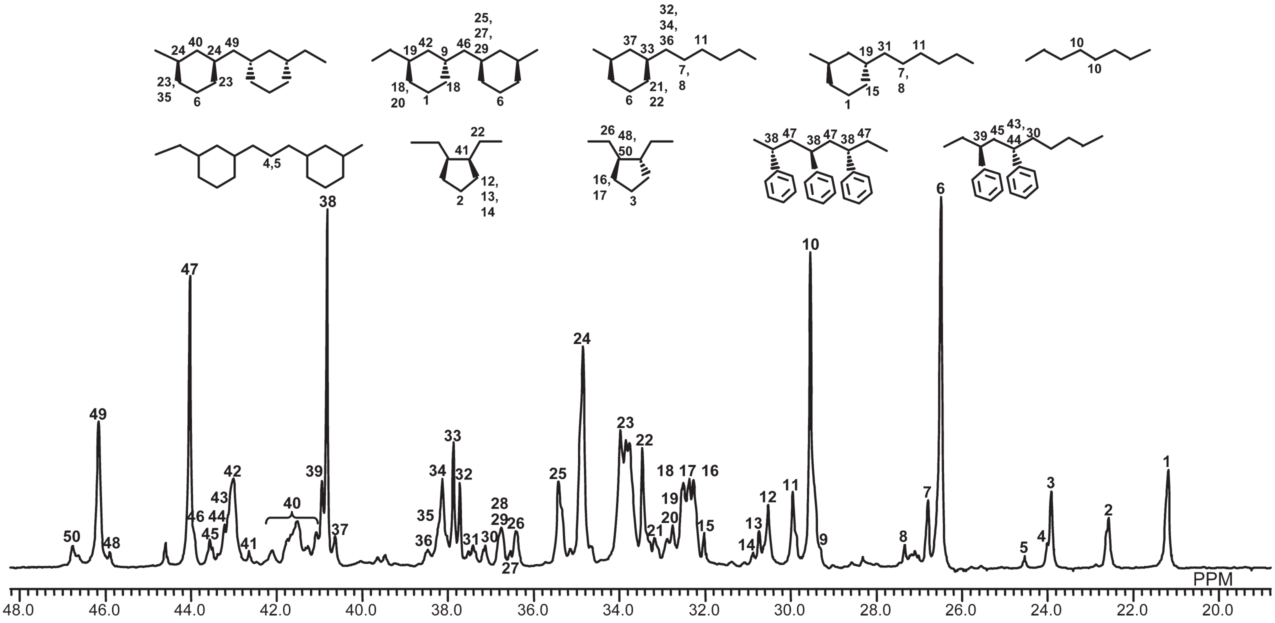
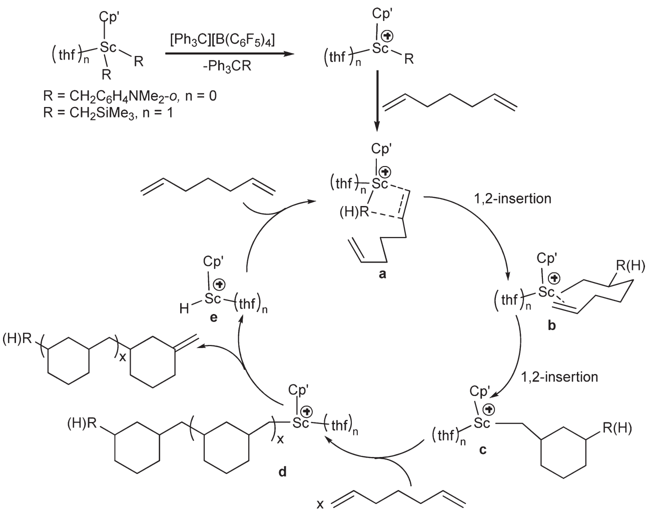


Figure 1. Aliphatic part of the ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2) of a HPD–ethylene–styrene terpolymer obtained in run 10, Table 1.

and styrene did not take place, and only a mixture of homopoly(HPD) and syndiotactic homopolystyrene was obtained, probably because these two monomers are too bulky to be directly connected (Table 1, run 6). It is also noteworthy that the increase of the feeding amount of both HPD and styrene under 1 atm of ethylene led to significant increase of the catalytic activity (product yield) and the molecular weight of the terpolymer product (Table 1, run 11). The GPC curves of all the terpolymers are unimodal with narrow molecular weight distribution, indicating the predominance of a single-site active catalyst species.

Because no NMR information on HPD–ethylene–styrene terpolymers could be found in the literature, we then carried out a detailed characterization of our copolymer products by the ^{1}H, ^{13}C, DEPT-^{13}C, HSQC, H2BC, and HMBC NMR analyses (see

Scheme 1. A Possible Mechanism for the Cyclopolymerization of 1,6-Heptadiene (HPD) Catalyzed by Scandium Complexes[13]



Supporting Information) to establish the comonomer incorporation and distribution in the copolymer chains. It was revealed that the HPD–ethylene copolymers are random (multiblock) copolymers containing MCH blocks, ethylene blocks, MCH–ethylene sequences, and ECP units (see Supporting Information). The HPD–ethylene–styrene terpolymers are also random (multiblock) copolymers. The terpolymers contained both the structure sequences observed in the HPD–ethylene copolymers and also syndiotactic styrene–styrene blocks and ethylene–styrene sequences (see Figure 1 and Supporting Information). No signals were attributed to HPD–styrene sequences, which is in agreement with the failure of HPD–styrene copolymerization as described above.

The differential scanning calorimetry (DSC) demonstrated that all of the terpolymers have high T_m (around 250 °C) (Table 1, runs 7–11), in agreement with the existence of syndiotactic polystyrene sequences.[11a]

Scheme 1 shows a possible mechanism of the cyclopolymerization of HPD,[13] which could also account for the influence of the THF ligand observed in the homopolymerization and copolymerization of HPD. The formation of a cationic scandium alkyl species from the reaction of a dialkyl precursor such as **1** or **2** with a borate compound such as $[Ph_3C][B(C_6F_5)_4]$ has been well documented previously.[10–12] The coordination of a C=C double bond of HPD to the cationic metal center could give the adduct complex **a**. The nucleophilic addition of the Sc–alkyl bond to the coordinated vinyl group in **a** in a 1,2-fashion would give **b**. The subsequent intramolecular insertion (cyclization) of the remaining C=C double bond in a 1,2-fashion should yield the MCH species **c**. The continuous insertion of HPD (chain propagation) in a similar way then gives **d**, which upon β-H elimination would release the polymer with a 3-methylenecyclohexane end-group and generate a scandium–hydride species (**e**) capable of propagating a new polymer chain. In the case of the THF-coordinated complex **1**, the coordination of a HPD monomer to the metal center (e.g., in **d**) could be retarded by the THF ligand, which would therefore slow down the chain propagation and give more chances for the β-H elimination (chain termination). If the intramolecular coordination of a C=C double bond is hampered by the THF ligand (e.g., in **b**), the formation of polymers with side chains having a terminal C=C double bond would be possible, which might therefore cause cross-linking reactions. This scenario could explain why the THF-free complex **2** is more selective than the THF-containing complex **1** in both homopolymerization and copolymerization of HPD.

In summary, the cycloterpolymerization of HPD with ethylene and styrene has been achieved for the first time by use of a half-sandwich scandium catalyst such as **2** to afford a new series of polymer materials having unique microstructures (five- and six-member ring cyclic units and syndiotactic polystyrene blocks) which are difficult to prepare by other means. The different performance observed between **1** and **2** suggests that a subtle change in the ligand environment of the catalyst metal center can significantly alter the polymerization process. Further studies on the polymerization and copolymerization of nonconjugated dienes by rare earth catalysts are in progress.

■ 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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(13) Only the pathway for the formation of the six-member ring MCH units is shown in Scheme 1 for clarity. The five-member ring ECP units could be formed by an initial 2,1-insertion of a C=C double bond of HPD followed by the intramolecular 1,2-insertion (cyclization) of the remaining C=C double bond (see Supporting Information).