Polymerization Catalysts

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Highly Isospecific Styrene Polymerization Catalyzed by Single-Component Bridged Bis(indenyl) Allyl Yttrium and Neodymium Complexes**

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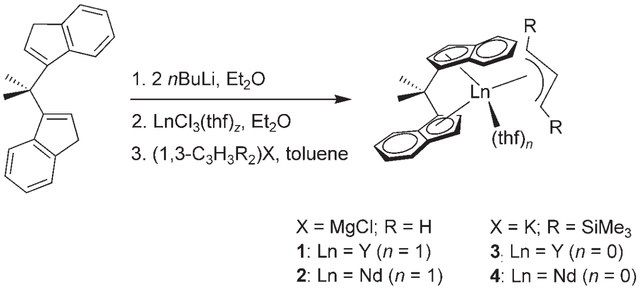
Polystyrene is a commodity polymer that can be obtained by many different mechanisms, that is, radical, cationic, anionic, and coordinative-insertive catalysis, with the latter technique being the best one for achieving precise control of the microstructure. Thus, syndiotactic polystyrene (sPS) has been effectively prepared with homogeneous cationic half-titanocene catalysts,[1] as well as Group 3 metal catalysts such as Hou's cationic half-scandocene[2] and neutral discrete [(CpCMe$_2$Flu)Ln(allyl)(thf)] complexes (Cp = cyclopentadienyl; Flu = 9-fluorenyl; Ln = Nd, Y; allyl = C_3H_5) that we recently introduced.[3] On the other hand, isotactic polystyrene (iPS) is still best produced by heterogeneous catalysis[4] or anionic polymerization.[5] Although a range of homogeneous catalysts have been reported to give isotactic-enriched polystyrene and oligomers,[6] there are very few examples of true single-site catalysts that form polystyrene isospecifically. Among those is the binary titanium-based system supported by a 1,4-dithiabutane-bridged bis(phenolato) (OSSO) ligand recently described by Okuda et al.[7,8] Herein, we report the synthesis of new ansa-bridged bis(indenyl) allyl yttrium and neodymium complexes [(IndCMe$_2$Ind)Ln(allyl)(ether)$_n$] (Ind = 2-indenyl; ether = Et$_2$O) as the first single-component catalysts for purely isospecific styrene homopolymerization.

At first, following a simple one-pot salt-metathesis procedure similar to that used for the synthesis of [(CpCMe$_2$Flu)Ln(allyl)(thf)] complexes,[3,9] we treated one equivalent of the dilithium salt of the isopropylidene-bridged bis(indenyl) ligand with the lanthanide chloride precursor, and further with allylMgCl to obtain the non-substituted allyl complexes **1** and **2** (Ln = Y, Nd, respectively; Scheme 1). Unfortunately, upon purification, complexes **1** and **2** became poorly soluble in usual solvents (aliphatic and aromatic hydrocarbons, THF), which hampered their detailed characterization by NMR spectroscopy.[10] Also, we could not isolate single crystals of **1** or **2** suitable for X-ray diffraction. Elemental analyses, as well as the ^{1}H NMR spectra of crude complexes **1** and **2** although complicated as a result of fluxional behavior and paramagnetism, are consistent with the presence of one coordinated THF molecule, which is in line with related complexes bearing the [CpCMe$_2$Flu]$^{2-}$ ligand.[3a,b]



Scheme 1. Synthesis of allyl complexes **1**–**4**.

The introduction of an allyl moiety that bears bulky 1,3-trimethylsilyl groups (using the corresponding potassium salt) allowed us to obtain the THF-free complexes **3** and **4** (Scheme 1). Contrary to their non-substituted allyl congeners **1** and **2**, complexes **3** and **4** are readily soluble in aromatic and aliphatic hydrocarbons. The diamagnetic yttrium complex **3** was fully characterized by NMR spectroscopy and an X-ray diffraction study (Figure 1).[11] In the solid state, complex **3** features trigonal geometry, with *rac* coordination of the bis(indenyl) ligand. The allyl group is η^3-coordinated with the SiMe$_3$ groups arranged in a *syn,syn* fashion; that is, the same conformation as in [{η^3-1,3-C$_3$H$_3$(SiMe$_3$)$_2$}$_2$Sc(μ-Cl)$_2$Li(thf)][12] and [{η^3-1,3-C$_3$H$_3$(SiMe$_3$)$_2$}$_2$Ca(thf)$_2$].[13] The Y–Cp(indenyl) distances (2.331 and 2.341 Å) are slightly shorter than those observed in {(2,4,7-Me$_3$Ind)$_2$YH}$_2$ (2.343–2.368 Å).[14] As a result of the short, rigid isopropylidene bridge, the bite angle Cp$_{\text{cent}}$-Y-Cp'$_{\text{cent}}$ is also smaller (113.33° compared to 131.87° and 132.4° for the latter unbridged bis(indenyl) complex). The ^{1}H NMR ([D$_6$]benzene, 298 K) spectrum of complex **3** (recrystallized or not) is consistent with exclusive *rac*

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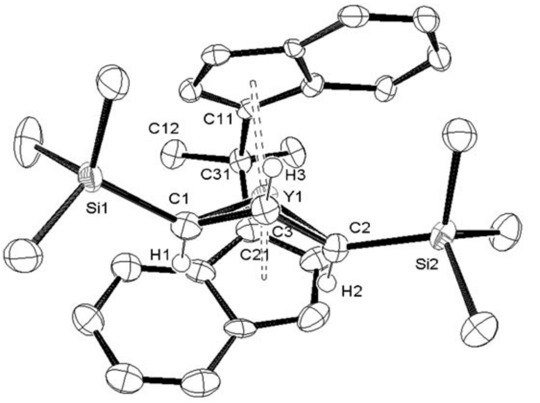

Figure 1. ORTEP view of the crystal structure of [(IndCMe$_2$Ind)Y-{1,3-(SiMe$_3$)$_2$C$_3$H$_3$}] (**3**). Ellipsoids are drawn at 50% probability; hydrogen atoms, except for allylic hydrogen atoms, are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–C1 2.576(5), Y1–C2 2.566(4), Y1–C3 2.583(4); C1-C3-C2 126.0(4), C21-C31-C11 102.4(3).

Table 1: Isospecific styrene (S) homopolymerization catalyzed by allyl complexes **1**–**4**.[a]

Run	Cat.	[S]/[Ln]	T [°C]	t [min]	Conv [%]	Activity[b]	M_n[c]	M_w/M_n[c]
1	**1**	600	60	30	57	66	65	1.4_9
2	**1**	500	80	15	87	181	58	1.8_5
3	**1**	1200	80	20	37	135	74	1.8_5
4	**1**	500	100	5	92	527	26	1.7_2
5	**1**	400	120	5	88	463	28	2.0_3
6	**2**	600	60	45	56	49	102	1.5_7
7	**2**	600	100	5	43	307	52	1.6_0
8	**3**	450	60	8	11	39	59	2.2_4
9	**3**	460	80	4	95	685	46	2.4_1
10	**3**	4600	80	21	78	1066	35	2.5_6
11	**3**	420	100	2	98	1279	22	2.5_3
12	**3**	480	120	2	100	1637	12	3.4_5
13	**4**	500	60	8	100	392	71	2.6_3
14	**4**	520	80	6	100	600	56	2.5_1
15	**4**	480	100	5	100	1094	36	2.2_7

[a] General conditions: Ln (12–40 μmol), total volume 1–20 mL, [S] = 8.70 M (neat). [b] Overall activity in kg(PS) mol(Ln)$^{-1}$ h^{-1}. [c] M_n [10^3 g mol^{-1}] and M_w/M_n values determined by GPC versus PS standards; subscripts in the M_w/M_n values show the uncertainty in the data.

coordination of the [IndCMe$_2$Ind]$^{2-}$ ligand (i.e., free of the *meso* stereoisomer)[15] and a solution structure similar to that observed in the solid state.[16] The allyl moiety appears as a triplet at $\delta = 7.00$ ppm for the central hydrogen and two doublets of doublets at $\delta = 3.85$ and 1.19 ppm for the non-equivalent terminal hydrogen atoms. Both methyl and trimethylsilyl groups appear each as two singlets, which reflects the global asymmetry of the molecule. Unlike its non-substituted allyl analogues, complex **3** does not exhibit a dynamic behavior in the temperature range 213–353 K.[17]

Styrene polymerizations were carried out with complexes **1**–**4**, at 60–120 °C, in the absence of any co-activator or scavenger. All complexes were found to be active, giving pure iPS (see below). Polymerizations were typically performed in bulk styrene (see Table 1 for representative results), though similar performances were observed in concentrated (i.e., 4.35 M) styrene solutions in cyclohexane or heptane (see Table S3 in the Supporting Information). On the other hand, introduction of toluene in the polymerization medium was found to be detrimental to the catalyst activity.[3] The overall activity of the new catalysts is in the range 40–1600 kg(iPS) mol(Ln)$^{-1}$ h^{-1} and expectedly increases with temperature. Note that the catalysts appear to be stable at least up to 120 °C, which is important from the point of view of industrial processes.[18] Yttrium complex **1** proved to be more active than its neodymium congener **2**, though the difference was less marked for the substituted allyl catalysts **3** and **4**. This trend in activity contrasts with our previous observations on syndiospecific styrene polymerization with [(CpCMe$_2$Flu)Ln(allyl)(thf)] catalysts, for which a dramatic difference between neodymium (most active) and yttrium (very poorly active) complexes was observed.[3]

GPC traces of the polymers were all monomodal with moderately narrow molecular-weight distributions, indicative of single-site behavior. Catalysts **1** and **2** induced narrower polydispersities than **3** and **4** (typically, $M_w/M_n = 1.5$–2.0 vs. 2.2–2.6, respectively), a feature that could be tentatively assigned to an easier initiation thanks to a less bulky allyl group in the former case.[19] The experimental number-average molecular weights, M_n, are systematically lower than the values calculated from the monomer-to-catalyst ratio and conversion, reflecting a moderate initiation efficiency in all cases. Expectedly, higher polymerization temperatures induce a decrease of the M_n values and a slight broadening of the polydispersities. The controlled nature of these systems was confirmed by the monotonous dependence of the molecular weights M_n with monomer conversion at 60–80 °C; for example, for the neodymium catalyst **2**, the M_n values increase almost linearly, at least in the first stage of the polymerization, but for the yttrium catalyst **1** the values show a saturation limit (see Figure S5 in the Supporting Information), likely reflecting that transfer to the monomer occurs to a significant extent under those conditions.

The microstructure of the polystyrenes was determined by high-field ^{13}C{^{1}H} NMR spectroscopy, which revealed a highly isotactic nature (confirmed by the melting temperature, T_m, of 219 °C, as determined by differential scanning calorimetry). A typical spectrum of an unfractionated polymer is shown in Figure 2, which presents a single sharp resonance at $\delta = 146.5$ ppm for the phenyl *ipso* carbon atom. According to the literature,[20] this sharp resonance is unambiguously attributed to the *mmmmmm* heptad. Remarkably, no stereo-error could be detected in the ^{13}C{^{1}H} NMR spectra, even those of polystyrenes produced at high temperatures (100–120 °C; see Figure 2). Usually, in olefin polymerization catalysis, such stereoerrors appear at higher temperatures and the way they are replicated (e.g., *mmmrmm*) or corrected (e.g., *mmmrrm*) are diagnostic of the stereocontrol mechanism, that is, chain-end (as for syndiospecific styrene polymerization[1–3]) or enantiomorphic control.[21] The unprecedented stereocontrol of our systems does not allow us to perform such statistic analysis, and we can only speculate at this moment, considering the *rac* coordination of the

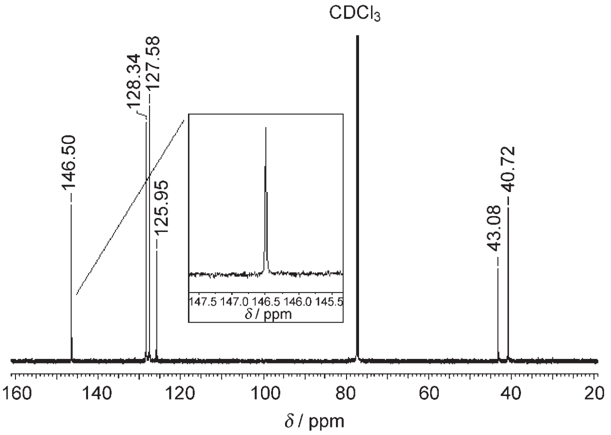

Figure 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C) spectrum of a crude iPS sample produced at 120 °C (Table 1, run 5).

$[IndCMe_2Ind]^{2-}$ ligand framework, that an enantiomorphic site control is operative.

Apart from the origin of the stereocontrol, the global data are consistent with a mechanism closely related to that proposed for the syndiospecific polymerization of styrene with the parent neutral ansa-lanthanidocenes $[(CpCMe_2Flu)Ln(allyl)(thf)]$.[3] In particular, the role of the allyl group appears essential for the initiation step.[19] The absence of an induction period observed for both catalysts **1** and **2** (see Figure S4 in the Supporting Information) suggests that displacement of coordinated THF by styrene is fast. For the sterically crowded allyl complexes **3** and **4**, we assume that coordination of styrene is connected to a haptotropic η^3–η^1 shift of the allyl group.[22]

In conclusion, we have reported a selective synthesis of *rac* ansa-bis(indenyl)lanthanide allyl complexes by a classic salt-metathesis protocol. These species turned out to be efficient single-component catalysts for the highly isospecific polymerization of styrene operable under industrially relevant conditions (bulk, 60–120 °C). The efficient control over the polymerization process peculiar to this unique catalytic system allows the preparation of highly stereoregular polymers with a broad range of molecular weights and distributions. Detailed mechanistic investigations on this new system are currently underway.

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[11] X-ray crystal structural data for complex **3**: $C_{30}H_{39}Si_2Y$, $M_r = 544.70$, $T = 100$ K, crystal size $0.24 \times 0.17 \times 0.10$ mm^3, orthorhombic, $P2_12_12_1$ (no. 19), $a = 10.1236(6)$, $b = 12.2158(7)$, $c = 23.5156(12)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $U = 2908.1(3)$ Å^3, $\rho_{calcd} = 1.244$ g cm^{-3}, $\mu = 2.1032$ mm^{-1}, 64252 collected, 6653 unique ($R_{int} = 0.0713$), final $R_1 = 0.0523$, wR_2 ($I > 2\sigma(I)$) = 0.1193, residual electron density extremes were 0.95 and -0.443 e Å^{-3}. CCDC-648472 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] MALDI-TOF mass spectrometry and ^{1}H NMR analyses of the polymer showed that the initiating group was, as expected, an allyl group (see Supporting Information). Note, however, that it was not possible to distinguish unambiguously between a $CH_2{=}CH{-}CH_2{-}CHPh$ or $CH_2{=}CH{-}(CH_2)_2{-}CHPh$ group, and thus to assess the regioselectivity (1,2- or 2,1-insertion mode) of the first insertion of styrene. The absence of any detectable head-to-head sequence in the ^{13}C NMR spectrum suggests that the polymerization is highly regiospecific in either the initiation step or the propagation step. Simple steric considerations in the case of the bulky 1,3-$(SiMe_3)_2$allyl groups call necessarily for a 2,1-insertion.

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