Highly Syndiospecific Polymerization of Styrene Catalyzed by Allyl Lanthanide Complexes

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Syndiotactic polystyrene (sPS) is a relatively new engineering material with unique properties. Since its discovery by Idemitsu Co. in 1985, syndiospecific polymerization of styrene has been intensively investigated.[1] Homogeneous two-component monocyclopentadienyl systems Cp*TiCl₃/MAO[1a] and Cp*TiMe₃/B(C₆F₅)₃[1b] constitute the most active precursors, affording sPS with high contents of r pentads ($rrrr > 90\%$). Tremendous efforts have been made to expand the niche of titanocenes[2] or to move away from Cp derivatives by introducing alkoxy- and amido ligation.[3] Styrene polymerization mediated by organogroup 3 complexes has been much less explored. The latter species are isovalent but not isoelectronic, with the Ti(III) true active species formed upon activation of Ti(IV) precursors with ionizing cocatalysts.[4] Among recent studies,[5] only a few examples of lanthanide-based catalysts have appeared to be significantly active for styrene polymerization,[6] and *atactic* polymers were produced in all the cases. Stereospecific variants of styrene polymerization mediated by organolanthanides are also known, giving poorly stereoregular materials (r or $m < 80\%$).[7] Nevertheless, controlled, highly stereospecific polymerization of styrene by organolanthanides has not been achieved thus far. Herein we report the synthesis of new neutral *ansa*-metallocene allyl complexes of early lanthanides based on the [Flu−CMe₂−Cp]²⁻ ligand, a framework that has been successfully developed for syndiospecific propylene polymerization.[8] Those new allyl lanthanidocenes show high activity in styrene polymerization, providing high syndiotacticity and good control of the polymerization.

The reaction of the anionic complex [(Cp−CMe₂−Flu)YCl₂]⁻-[Li(ether)₄]⁺ (ether = Et₂O, THF) (1)[9] with the Grignard reagent ClMgC₃H₅ (1 equiv vs Ln, as a THF solution) in toluene at 20 °C cleanly gives the neutral allyl complex [Flu−CMe₂−Cp]Y(C₃H₅)-(THF) (2) as a yellow microcrystalline powder. The parent La (3), Nd (4), and Sm (5) complexes were prepared analogously (Scheme 1). Compounds 2−5 were characterized by elemental analysis and NMR spectroscopy (for diamagnetic species). Single crystals of 2[10] and 4 (Figure 1) were analyzed by X-ray diffraction.

The molecule of 4 contains a chiral neodymium atom that is coordinated in a pseudo-tetrahedral fashion by a chelating Cp−Flu moiety, an allyl group, and a THF molecule. Taking into account the Nd−C bond distances, the fluorenyl moiety may be in a way of approaching an η^3-bonding mode by the central five-membered ring, as observed before for a set of fluorenyl complexes.[9,11] Complex 4 features a very narrow bite angle Cp_{cent}−Nd−Flu$'_{cent}$ of 93.88°, which is ca. 10° lower than in known [Cp−CR₂−Flu]LnX complexes of early lanthanides.[9] The allyl fragment
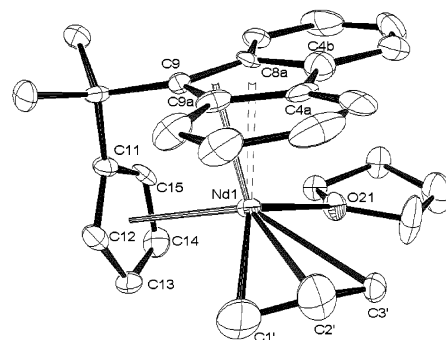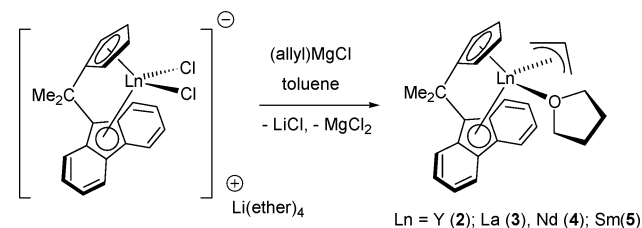
Figure 1. ORTEP structure of 4 (thermal ellipsoids at the 30% level; hydrogen atoms removed). Selected bond lengths (Å): Nd−C(1) 2.656(9), Nd−C(2) 2.699(11), Nd−C(3) 2.725(12), Nd−C(8A) 2.765(9), Nd−C(9) 2.673(8), Nd−C(9A) 2.825(10), Nd−C(4A) 2.982, Nd−C(4B) 2.935(9).

Scheme 1

is η^3-bonded with the three carbon atoms displaying nearly equal participation.

Styrene polymerization was attempted with complexes 2−5 under mild conditions ($T = 20-60$ °C, bulk or toluene solution) in the absence of scavenger and was found to give highly sPS. Representative results are reported in Table 1. The polymerization activity of the allyl complexes is in the order Nd ≫ Sm > La > Y, the Nd complex 4 featuring a remarkably high activity (entries 7−9). The styrene polymerization reactions mediated by allyl complexes 2−5 all feature an induction period of a few minutes (entries 6−11; see the Supporting Information). Also, when the polymerization temperature is increased from 50 to 60 °C, a significant increase in activity is observed, which is greater than that expected from the simple influence of temperature on kinetics. These observations suggest the existence of a preactivation step, possibly related to dissociation of the THF molecule from the metal center in the precatalyst.

Polymerizations of bulk styrene led to 70−85% maximum monomer conversions,[12] while introduction of toluene in the polymerization medium, which could act as a solvent media for the monomer, was found detrimental for catalyst activity.[13] The average number molecular weights (M_n) range from 10 000 up to 135 000, the higher polymers having been prepared with the most productive Nd complex 4 (entries 12 and 13). The molecular weight

Table 1. Styrene Homopolymerization Catalyzed by Allyl Lanthanide Complexes [Cp−CMe₂−Flu]Ln(C₃H₅)(THF) (**2**−**5**)^a

entry	complex	time (min)	yield^b	activity^c	$M_n \times 10^{-3}$	M_w/M_n	T_m (°C)
1^d	**2**	20	8	13	15	1.64	262
2^d	**2**	40	20	17	19	1.84	262
3^d	**2**	60	26	14	22	1.92	262
4^d	**2**	120	41	11	23	2.15	263
5^e	**3**	5	16	118	20	1.22	257
6^e	**4**	2.5	11	448	21	1.25	262
7^e	**4**	3.5	34	989	35	1.31	nd
8^e	**4**	4	45	1145	50	1.28	261
9^e	**4**	5	84	1710	54	1.73	264
10^f	**4**	5	9	256	62	1.50	nd
11^f	**4**	10	64	911	nd	nd	nd
12^f	**4**	30	72	342	135	2.09	263
13^g	**4**	30	28	222	128	2.60	nd
14^e	**5**	5	28	218	27	1.49	262
15^h	**Ti-MAO**^{h}	2	76	102 000	76	2.15	263

^{a} General conditions: 4−5 × 10^{-5} mol of Ln complex; 8.65 mol·L^{-1} (bulk) of styrene at 60 °C; nd = not determined. ^{b} Isolated yield (%) of sPS collected after precipitation in MeOH. ^{c} In kg sPS·mol cat^{-1}·h^{-1}. ^{d} In 5 mL of toluene; [St]/[Ln] = 800. ^{e} [St]/[Ln] = 600. ^{f} [St]/[Ln] = 2300. ^{g} [St]/[Ln] = 4000. ^{h} CpTiCl₃/MAO system; 8.65 mol.L^{-1} (bulk) of styrene at 60 °C; [styrene]/[Ti] = 4500; [Al]/[Ti] = 1000.

145.6 ppm
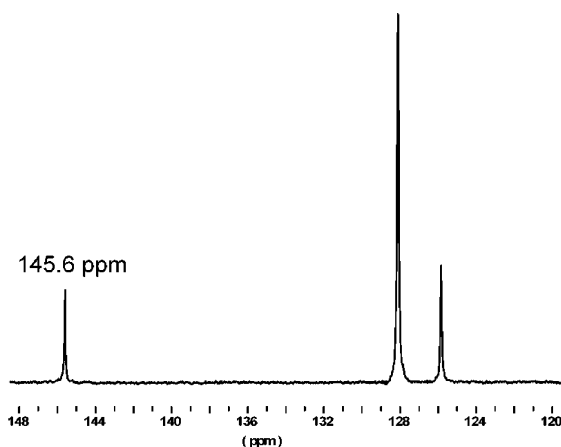
Figure 2. Aromatic region of the ^{13}C{^{1}H} NMR spectrum (125 MHz, 60 °C, CDCl₃) of sPS obtained with complex **4** (entry 9).

distributions are rather narrow, ranging usually from 1.25 to 2.10, indicating a single-site behavior of the catalyst. Larger polydispersities (2.1 < M_w/M_n < 3.2) have been determined only for sPS samples produced over relatively long periods and/or at higher monomer-to-catalyst ratios (e.g., entries 4 and 13), which may arise from gradual catalyst decomposition with time. Experimental M_n values are systematically lower than those calculated (for M_w/M_n < 1.3), reflecting a moderate initiation efficiency. The dependence of the molecular weights M_n vs yields appears approximately linear in the first stage of the polymerization but shows afterward a saturation limit (see the Supporting Information).

Remarkably, the microstructure of the polystyrenes obtained with all these allyl lanthanide complexes is highly syndiotactic, giving a *rrrr* pentad abundance of ≥99% as determined by ^{13}C NMR (Figure 2).^{2b} The high syndiotacticity of the polystyrenes is also illustrated by the high T_m of 250−269 °C, values typically found for sPS.^{2a} Also, the glass transition temperature (T_g = 111.5 °C) and the Young modulus (E = 2320 MPa at 35 °C), both determined by DMA (entry 11), compare well with the corresponding values determined under the same conditions (T_g = 110.8 °C; E = 2920 MPa at 30 °C) for an sPS sample prepared independently with the CpTiCl₃/MAO system (entry 15).

In conclusion, we have disclosed a new class of neutral allylic organolanthanide derivatives bearing a fluorenyl-based ligand environment that displays high activity in the polymerization of styrene under mild conditions. These single-component species afford highly syndiotactic polystyrene. We are currently studying the influence of ligand parameters and the stereocontrol mechanism; preliminary investigations indicate a chain-end control, as usually observed in syndiotactic polymerization of styrene.^{1b,c,4a}

Supporting Information Available: Experimental procedures for the preparation of lanthanide allyls **2**−**5**, polymerization procedure and kinetics, polymer analysis data, crystallographic data for **4**, including final coordinates, thermal parameters, bond distances, and bond angles (CIF, PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464−2465. (b) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593−6594. (c) Po, R.; Cardi, N. *Prog. Polym. Sci.* **1996**, *21*, 47−88. (d) Tomotsu, N.; Ishihara, N.; Newman, T. H.; Malanga, M. T. *J. Mol. Catal. A* **1998**, *128*, 167−190. (e) Yokota, K.; Inoue, T.; Shozaki, H.; Tomotsu, N.; Kuramoto, M. Ishihara, N. In *Metalorganic Catalysts for Synthesis and Polymerisation*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, Heidelberg, 1999; p 435. (f) Ishihara, N. In *Progress and Development of Catalytic Olefin Polymerization*; Sano, T., Uozumi, T., Nakatani, H., Terano, M., Eds.; Technology and Education Publishers: Tokyo, 2000, p 121.

(2) (a) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356−3360. (b) Wang, Q.; Quyoum, R.; Gillis, D. J.; Tudoret, M.-J.; Jeremic, D.; Hunter, B. K.; Baird, M. C. *Organometallics* **1996**, *15*, 693−703. (c) Knjazhanski, S. Y.; Cadenas, G.; Garcia, M.; Perez, C. M.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Lyssenko, K. *Organometallics* **2002**, *21*, 3094−3099.

(3) (a) Zambelli, A.; Oliva, L.; Pellecchia, C. *Macromolecules* **1989**, *22*, 2129−2130. (b) Liguori, D.; Centore, R.; Tuzi, A.; Grisi, F.; Sessa, I.; Zambelli, A. *Macromolecules* **2003**, *36*, 5451−5458. (c) Capacchione, C.; Proto, A.; Ebeling, H.; Mullhaupt, R.; Moller, K.; Spaniol, T.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964−4965.

(4) (a) Pellecchia, C.; Grassi, A. *Top. Catal.* **1999**, *7*, 125−132. (b) Mahanthappa, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12093−12094.

(5) (a) Thomas, R. R.; Chebolu, V.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096−4103. (b) Shen, Z. *Polym. J.* **1990**, *22*, 919−924. (c) Khvostov, A. V.; Belsky, V. K.; Sizov, A. I.; Bulychev, B. M.; Ivchenko, N. B. *J. Organomet. Chem.* **1997**, *531*, 19−25. (d) Yuan, F.; Shen, Q.; Sun, J. *J. Organomet. Chem.* **1997**, *538*, 241−245. (e) Hultzsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228−243. (f) Bogaert, S.; Carpentier, J.-F.; Chenal, T.; Mortreux, A.; Ricart, G. *Macromol. Chem. Phys.* **2000**, *201*, 1813−1822.

(6) Hou, Z.; Zhang, Y.; Tezuka, H.; Xie, P.; Tardif, O.; Koizumi, T.-A.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10533−10542.

(7) (a) Baudry-Barbier, D.; Camus, E.; Dormond, A.; Visseaux, M. *Appl. Organomet. Chem.* **1999**, *13*, 813−817. (b) Tanaka, K.; Furo, M.; Ihara, E.; Yasuda, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1382−1390.

(8) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256. (b) Alt, H.; Kopple, A. *Chem. Rev.* **2000**, *100*, 1205−1221.

(9) (a) Kirillov, E.; Toupet, L.; Lehmann, C. W.; Razavi, A.; Kahlal, S.; Saillard, J.-Y.; Carpentier, J.-F. *Organometallics* **2003**, *22*, 4038−4046. (b) Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *Organometallics* **2004**, *23*, 2768−2777.

(10) Usual data refinement enabled to confirm the atom connectivity of **2**. However, the poor final *R* factor value does not allow us to discuss geometrical parameters (bond lengths and angles).

(11) Lee, M. H.; Hwang, J.-W.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 5124−5129.

(12) Since sPS is not soluble under the reaction conditions and precipitated during polymerization, mass transfer limitations likely take place, which may cause eventually reduction of the monomer conversion.

(13) Oliva, L.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1989**, *22*, 1642−1645.

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