8670 *Macromolecules* **2002,** *35,* 8670−8671

$[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2Ln(\mu\text{-}Me)_2Li(TMEDA)$ (Ln = Nd, Yb) as Effective Single-Component Initiators for Styrene Polymerization

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Received July 17, 2002

Revised Manuscript Received September 23, 2002

Well-defined organolanthanide complexes have shown excellent catalytic behavior, including high activity, high strereoselectivity, living polymerization ability, and no requirement for a cocatalyst in the polymerization of ethylene, acrylates, and lactones.[1] However, the styrene polymerization by organolanthanide complexes is in general quite difficult.[2−7] Recently, some modified lanthanide metallocene complexes by the replacement of one C_5Me_5 ligand for a monodentate anionic ligand, such as $[(C_5Me_5)Sm(THF)_m(ER)(\mu\text{-}C_5Me_5)K(THF)_n]$ (ER = OAr, SAr, NRR′, or PHAr),[8] $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}CH_2CH_2CH_2CH_2CH_2CH_3)]_2$,[9] and $La(C_5Me_5)[CH(SiMe_3)_2]_2(THF)$,[10] were developed as initiators for styrene polymerization. It is expected that the organolanthanide complexes supported by bidentate ligands without bulky C_5Me_5 ligand might offer a further more open ligand sphere and thus show higher catalytic activity toward sterically demanding styrene.

Guanidinate anions $[(RN)_2C(NR_2')]^-$, whose electronic properties and steric bulk can be easily modified through variation of the substituents on the nitrogen atoms, have just been attracted attention in organometallic chemistry of transition metals and lanthanide elements.[11−16] It was recently found that bis(guanidinate) Zr(IV) complexes had activity for ethylene homopolymerization and ethylene/1-hexene copolymerization,[15] and monoguanidinate aryloxo complexes of lanthanum were active for the ring-opening polymerization of lactide.[16] However, to the best of knowledge, nothing has been published on styrene polymerization by organometallic complexes supported by guanidnate ligands. On the basis of this situation and as a result of ligand-oriented catalyst design research, we chose guanidinate anions as a bidentate candidate. And, we discovered that guanidinate lanthanide methyl complexes are a new kind of effective single-component initiator for styrene polymerization. This communication reports these preliminary results.

The guanidinate lanthanide methyl complexes, $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2Ln(\mu\text{-}Me)_2Li(TMEDA)$ (Ln = Nd (**1**), Yb (**2**)), can be obtained as crystals in 72−76% yield by the reaction of $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2Ln(\mu\text{-}Cl)_2Li(THF)_2$ with 2 equiv of MeLi in hexane.[17] Full characterization by the X-ray analysis together with elemental analysis shows that **1** is a lanthanide−lithium bimetallic complex with two methyl bridges. The $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2Nd$ moiety is bonded through two methyl bridges to a lithium cation, which in turn is bonded to two nitrogen atoms of a TMEDA molecule (see Figure 1). Spectroscopic data imply that **2** should have the same molecular structure as **1**.[17]

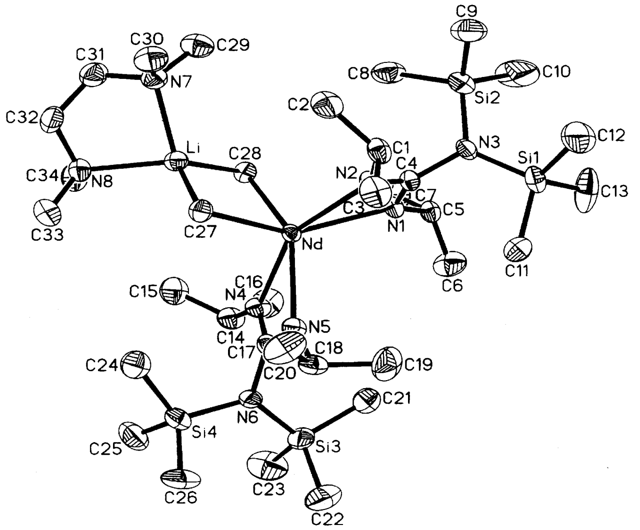

Figure 1. ORTEP diagram of $[(SiMe_3)_2NC(N\textit{i}Pr)_2]_2Nd(\mu\text{-}Me)_2Li(TMEDA)$ (**1**) showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Nd−N(1) 2.477(6), Nd−N(2) 2.513(6), Nd−N(4) 2.523(6), Nd−N(5) 2.476(7), Nd−C(27) 2.590(8), Nd−C(28) 2.595(8), Li−C(27) 2.215(16), Li−C(28) 2.244(15); N(1)−Nd−N(2) 53.5(2), N(5)−Nd−N(4) 54.0(2), C(27)−Nd−C(28) 89.3(2), C(27)−Li−C(28) 109.6(6), C(4)−Nd−Li 116.0(3), C(17)−Nd−Li 115.5(3), C(4)−Nd−C(17) 128.5(2).

As shown in Table 1, both complexes showed high activity for the styrene polymerization in the temperature range 70−100 °C within 10 min, while under the same conditions, thermal self-polymerization and MeLi initiation did not produce polymer (runs 12 and 13). The polymerization depends on temperature. When the temperature was decreased to 55 °C, only a trace amount of polymer was obtained (run 11). This reflects the high activation energy needed to initiate the polymerization. However, the yields decreased sharply to 67% by **1** and 57% by **2** when the polymerization temperature was 100 °C (runs 4 and 6). This may be due to partial deactivation of the initiators. The efficiencies of the present initiator system are quite high (>55%). Efficiencies above 100% observed may be due to chain transfer reactions. All of the GPC curves of the polystyrenes were unimodal. These polystyrenes had narrow molecular weight distributions ($M_w/M_n < 2$) with molecular weights (M_n) ranging from 1.72×10^4 to 5.89×10^4. The molecular weight distribution became broader with increasing polymerization temperature. The yields or reaction rates of the polymerizations using **1** and **2** are nearly equal. The catalytic activity of the present polymerization systems ($>1 \times 10^2$ kg/(mol h)) is higher than those of organolanthanide species reported in the literature.[3−10] The darkening of the color of the reaction mixture during the polymerization reactions indicates that the phenyl ring of styrene transfers π-electrons to the lanthanide center.

Triad microstructural analysis of the resulting polystyrene using ^{1}H NMR indicates that the polymerization system produces atactic/syndiotactic-rich polystyrenes, and microstructures enrich in syndiotacticity. The syndiotacticity decreases with increasing polymerization

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10.1021/ma0211380 CCC: $22.00

Table 1. Polymerization of Styrene with [(SiMe$_3$)$_2$NC(NiPr)$_2$]$_2$Ln(μ-Me)$_2$Li(TMEDA) (Ln = Nd (1), Yb (2))[a]

run	initiator	T (°C)	[M$_0$]/[I]$_0$	yield (%)[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]	rr (%)	efficiency (%)[d]	activity[e] (kg/(mol h))
1	**1**	70	290	98	1.72	1.60		58	177
2	**1**	70	400	94	2.33	1.59		60	236
3	**1**	70	470	79	4.19	1.39	49	108	232
4	**1**	100	470	67	2.02	1.84	31	62	197
5†	**1**	70	400	92	2.27	1.46		59	463
6	**2**	100	470	57	4.08	2.01		146	168
7	**2**	70	470	96	5.89	1.80	53	126	284
8	**2**	70	300	98	3.88	1.90		127	184
9*	**2**	85	470	96	4.12	1.88		88	939
10	**2**	85	470	96	3.99	1.95	28	85	281
11	**2**	55	470	trace					
12		85		0	0	0	0	0	0
13	MeLi	85	300	0	0	0	0	0	0

[a] General polymerization conditions: in toluene; monomer/solvent = 1:1 (v/v); 10 min; †5 min; *3 min. [b] Yield = weight of polymer obtained/weight of monomer used. [c] Measured by GPC calibrated with polystyrene standards. [d] Defined as the percentage of active initiators, calculated from the observed number of polymer chains relative to the theoretical ones, assuming that each lanthanide complex initiates one polymer chain. [e] Activity of catalyst, kg of polystyrene/(mol of catalyst h).

temperature. For example, raising the polymerization temperature from 70 to 85 °C decreases the syndiotactic content from 53 to 28% using **2** as initiator.

In summary, we give the first example of styrene polymerization efficiently initiated by organolanthanide complexes with polydentate nitrogen-based ligand. Further studies on the polymerization mechanism and stereospecific polymerization are in progress.

Acknowledgment. We are indebted to the Chinese National Natural Science Foundation and the Department of Education of Jingsu Province for financial support.

Supporting Information Available: Experimental details and GPC profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Details of the synthesis and characterization of **1** and **2** are deposited as Supporting Information.

MA0211380