FULL PAPER

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A Lutetium Allyl Complex That Bears a Pyridyl-Functionalized Cyclopentadienyl Ligand: Dual Catalysis on Highly Syndiospecific and *cis*-1,4-Selective (Co)Polymerizations of Styrene and Butadiene

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Abstract: A novel linked-half-sandwich lutetium–bis(allyl) complex [(C_5Me_4–C_5H_4N)Lu(η^3-C_3H_5)$_2$] (**1**) attached by a pyridyl-functionalized cyclopentadienyl ligand was synthesized and fully characterized. Complex **1** in combination with [Ph_3C][$B(C_6F_5)_4$] exhibited unprecedented dual catalysis with outstanding activities in highly syndiotactic (*rrrr* > 99 %) styrene polymerization and distinguished *cis*-1,4-selective (99 %) butadiene polymerization, respectively. Strikingly, this catalyst system exhibited remarkable activity (396 kg copolymer $(\text{mol}_{\text{Lu}}\,\text{h})^{-1}$) for the copolymerization of butadiene and styrene. Irrespective of whether the monomers were fed in concurrent mode or sequential addition of butadiene followed by styrene, diblock copolymers were obtained exclusively, which was confirmed by a kinetics investigation of monomer conversion of copolymerization with time. In the copolymers, the styrene incorporation rate varied from 4.7 to 85.4 mol %, whereas the polybutadiene (PBD) block was highly *cis*-1,4-regulated (95 %) and the polystyrene segment remained purely syndiotactic (*rrrr* > 99 %). Correspondingly, the copolymers exhibited glass transition temperatures (T_g) around −107 °C and melting points (T_m) around 268 °C; typical values for diblock microstructures. Such copolymers cannot be accessed by any other methods known to date. X-ray powder diffraction analysis of these diblock copolymers showed that the crystallizable syndiotactic polystyrene (*syn*-PS) block was in the toluene δ clathrate form. The AFM micrographs of diblock copolymer showed a remarkable phase-separation morphology of the *cis*-1,4-PBD block and *syn*-PS block. This represents the first example of a lutetium-based catalyst showing both high activity and selectivity for the (co)polymerization of styrene and butadiene.

Keywords: allyl ligands • cyclopentadienyl ligands • lanthanides • polymerization • syndiotactic polymers

Introduction

Syndiotactic polystyrene (*syn*-PS), possessing a high melting point, high tensile modulus, and excellent physical properties,[1] is a promising thermoplastic and has potential application in engineering plastics. *syn*-PS was first discovered more than two decades ago by Ishihara et al. using the monocyclopentadienyl (Cp) titanium catalyst.[2] Subsequently, titanium analogues generally formulated as [Cp′TiX_3] (Cp′ = substituted Cp, X = halogen), [IndTiX_3] (Ind = indenyl), or [FluTiX_3] (Flu = fluorenyl) were invented and exhibited improvements in catalytic activity or syndioselectivity for styrene polymerization.[3] Compared with the achievements of titanium catalysts, rare-earth-metal catalysts have been noted for their inertness or low specific selectivity towards styrene polymerization. The stalemate was broken in 2004 by the discovery of the allyl *ansa*-neodymocene catalyst[4] and the half-sandwich scandium alkyl cationic catalyst system:[5] both displayed excellent activity to provide perfect *syn*-PS. These findings greatly stimulated researchers' interest, which led to the innovation of other scandium catalysts such as those attached to Cp′, hetero-Cp′, and Ind′ ligands.[6] Nevertheless, besides scandium—an element electronically close to titanium—and the only lanthanide neodymium, to

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date, other lanthanide elements have not been reported for syndiospecific styrene polymerization with obvious activity.

Meanwhile, *cis*-1,4-regulated polybutadiene (PBD), as a promising synthetic rubber, has attracted increasing attention owing to its excellent elastic properties.[7,8] Among the variety of catalyst systems reported, those based on rare-earth metals are superior with respect to the activity and the *cis*-1,4 selectivity to provide PBD with outstanding characteristics such as excellent abrasion and cracking resistance, and raw polymer strength as well as low gel formation.[9] Unfortunately, lutetium complexes have usually been found inert for butadiene polymerization with the only exception being the NCN-pincer aryldiimine-ligated lutetium dichloride system.[9f]

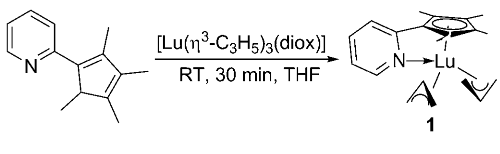
Considering the excellent properties of thermoplastic *syn*-PS and elastic *cis*-1,4-PBD, the specific selective copolymerization of styrene and butadiene has obvious advantages. *syn*-PS is crystalline and brittle and hard to process, which impede it from being an applicable material. The incorporation of highly *cis*-1,4-regulated PBD segments can greatly improve the toughness of *syn*-PS. On the other hand, when styrene–butadiene copolymers are used as rubber (SBR), the crystallizable *syn*-PS segments will act as a reinforcing agent for elastic *cis*-1,4-PBD to provide distinguished mechanical and chemical properties.[10] Moreover, the higher *cis*-1,4 content of PBD segments will efficiently improve the drawbacks of commercial SBR produced by anionic polymerization,[11] such as high thermogenesis, low elasticity, and low cold resistance[12] arising from *trans*-1,4- or 1,2-PBD blocks.

However, to date, few catalyst systems exhibit dual catalysis in the homopolymerization of styrene and butadiene with excellent selectivity. Although the copolymerization of styrene with butadiene or isoprene has been achieved by using some titanium and rare-earth-metal-based catalyst systems,[13–16] the problems such as low activity, or low styrene incorporation rate, or high *trans*-1,4- (or 1,2- or 3,4-) polydiene segments as well as relatively low molecular weights accompanied by broad molecular weight distributions (the presence of homopolymers) have not been well resolved. Therefore highly specific selective styrene–butadiene copolymerization has remained as a promising but challenging subject for academic and industrial fields.

Lanthanide–allyl complexes have been synthesized and have had their catalytic behavior extensively investigated,[17] however, their catalysis of syndiospecific polymerization of styrene has been explored less.[4] Herein we report the novel linked-half-sandwich lutetium–bis(allyl) complex [$(C_5Me_4-C_5H_4N)Lu(\eta^3-C_3H_5)_2$] (**1**) bearing a pyridyl-functionalized Cp ligand, which under the activation of [Ph_3C][$B(C_6F_5)_4$] shows unprecedented dual catalysis of the highly syndiospecific styrene polymerization and the distinguished *cis*-1,4-selective butadiene polymerization. More remarkably, the butadiene–styrene copolymerization can also be achieved with high activity to give diblock copolymers having variable styrene insertion rate, high and mono-modal molecular weight, and especially excellent regularities for both sequences. This represents the first example of a lanthanide-element-based precursor realizing highly specific selective (co)polymerizations of butadiene and styrene.

Results and Discussion

Preparation of complex 1: The straightforward protonolysis reaction of [$Lu(\eta^3-C_3H_5)_3(diox)$] (diox = 1,4-dioxane) and $C_5Me_4H-C_5H_4N$ in THF afforded the lutetium–bis(allyl) complex **1**, [$(C_5Me_4-C_5H_4N)Lu(\eta^3-C_3H_5)_2$], selectively (yield: 73%; Scheme 1). X-ray diffraction analysis revealed that complex **1** is a solvent-free monomer, in which the pyridyl-Cp ligand coordinates to the Lu^{III} ion in a η^5/κ^1 fashion, generating a constrained-geometry configuration (CGC), whereas the two allyl moieties coordinate to the Lu^{III} ion in $\pi-\eta^3$ modes, in which one allyl ligand adopts a prone orientation, and the other is supine (Figure 1). The ^1H NMR spectrum of **1** shows that the central allylic protons (methine) give a quintet around $\delta = 6.33–6.46$ ppm and the terminal allylic protons (methylene, H_{anti} and H_{syn}) exhibit a doublet at $\delta = 3.10$ ppm, which suggests equivalence of the *anti* and *syn* protons in the solution state at room temperature. Meanwhile the bite angle, Cp_{cent1}-Lu-N (84.1(3)°) in **1**, is much smaller than Cp_{cent1}-Y(1)-N(1) (95.4(3)°)[17a] and



Scheme 1. Synthesis of lutetium–bis(allyl) complex **1**.

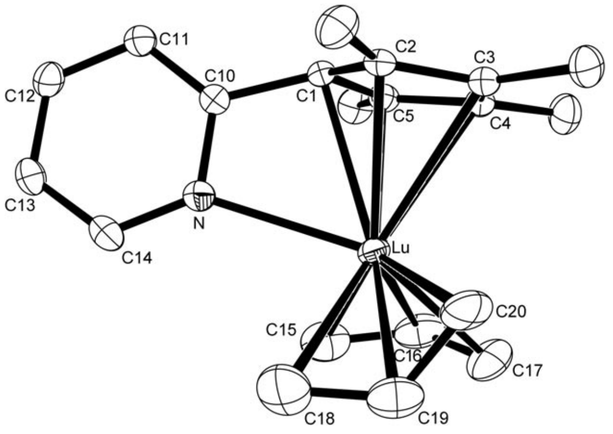


Figure 1. X-ray structure of **1** with 40% probability of thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu–C(Cp) (average) 2.613(3), Lu–Cp_{cent1} 2.318(2), Lu–C_{AT} (av.) 2.567(4), Lu–C_{AC} (av.) 2.603(3), Lu–N 2.452(3); C_{AT}-C_{AC}-C_{AT} 126.8(4), Cp_{cent1}-Lu-C_{cent2} 113.0(3), Cp_{cent1}-Lu-C_{cent3} 132.2(3), C_{cent2}-Lu-C_{cent3} 107.6(3), Cp_{cent1}-Lu-N 84.1(3). (C_{AT} = terminal allylic carbon atom. C_{AC} = central allylic carbon atom. Cp_{Cent1}, C_{Cent2}, and C_{Cent3} are the centroids of the cyclopentadienyl ring and the two allyl ligands, respectively).

Cp_{cent}-Y-Cp'_{cent} (113.33°) in the *ansa*-yttrocenes[18] (if the influence of the ionic radius is ignored), which suggests a wide opening environment around the Lu^{III} ion. The opening environment may contribute significantly to the high activity of complex **1** towards the polymerization of the bulky styrene (St) monomer (vide infra). It is noteworthy that complex **1**, although isolated from a solution in THF, has no coordinating THF molecules, which may be attributed to the concerted effects of the CGC of the pyridyl-Cp ligand and the π–η^3 coordinating allyl groups. Solvent-free complexes are highly favored by polymerization of nonpolar monomers, especially olefins.[19]

Homopolymerization of styrene and butadiene: We first investigated the styrene polymerization catalyzed by **1**/$[Ph_3C][B(C_6F_5)_4]$ in toluene at room temperature; the results are summarized in Table 1 (runs 1–4). Upon activation with $[Ph_3C][B(C_6F_5)_4]$, complex **1** showed a high activity of 1.56×10^3 kg$(mol_{Lu}h)^{-1}$ towards styrene polymerization to give polystyrene with perfect syndiotacticity (*rrrr* > 99 %) (Table 1, run 1), which could be confirmed by the strong and sharp singlets appearing at $\delta = 145.67$ (*ipso*-Ph), 45.04 (methylene), and 41.67 ppm (methine) in the ^{13}C NMR spectrum (Figure 3 in the Supporting Information) and by the strong endothermic peak appearing at 270 °C in the differential scanning calorimetry (DSC) curve (Figure 6 in the Supporting Information). More remarkably, with increased styrene loading from 250 to 1000 equiv, an activity up to 6.24×10^3 kg$(mol_{Lu}h)^{-1}$ was reached, which was comparable to the most active titanium and scandium systems reported (Table 1, runs 2–4).[5,6d,20] The resultant polystyrene retained its pure syndiotacticity (*rrrr* > 99 %), and the molecular weights increased linearly with the ratios, whilst the molecular weight distribution remained almost unchanged ($M_w/M_n = 1.88$–1.98). As far as we are aware, complex **1** represents the first lutetium-based active species for syndiospecific styrene polymerization with outstanding activity.

Intrigued by the above results, the performances of **1**/$[Ph_3C][B(C_6F_5)_4]$ in butadiene polymerization were also explored, which converted 500 equiv of butadiene into polybutadiene (PBD) in less than 1 min (Table 1, run 5). The resultant PBD had high *cis*-1,4 regularity (97.1 %) and a narrow molecular weight distribution ($M_w/M_n = 1.24$), which was consistent with the low glass transition temperatures (T_g) around −107 °C determined by DSC, the typical value for high *cis*-1,4-PBD. When the monomer loading was doubled and quadrupled, the molecular weight of the obtained PBD was almost doubled and quadrupled and the narrow molecular weight distribution remained unchanged, which indicated a living polymerization (Table 1, runs 6 and 7). That the polymerization was living could be further confirmed by adding another 500 equiv of BD to a 100 % conversion BD (500 equiv) polymerization system; a total 100 % conversion was achieved to give PBD with doubled molecular weight (Table 1, run 8). When the polymerization was performed in chlorobenzene instead of nonpolar toluene, the system showed decreased catalytic activity; to our delight, a perfect *cis*-1,4-regulated (99 %) PBD was obtained (Table 1, run 9), which could be evidenced by the very strong and sharp singlet appearing at $\delta = 27.42$ ppm in the ^{13}C NMR spectrum (Figure 5 in the Supporting Information), and correspondingly a much lower glass transition temperature appeared at −109 °C in the DSC curve.

Block copolymerization of butadiene and styrene: The excellent dual catalysis of **1**/$[Ph_3C][B(C_6F_5)_4]$ for both highly specific selective polymerizations of styrene and butadiene prompted us to attempt their copolymerization. The copolymerization was firstly performed in toluene at 20 °C for 10 min by the concurrent addition of two monomers under the styrene feeding molar fractions varying from 10 to 90 % (mol %). As shown in Table 2, high conversions (63–86 %) were obtained in the full range of monomer feeding ratios to reach distinguished high activities of 306–396 kg $(mol_{Lu}h)^{-1}$, which were remarkably higher than those reported to date (≈30 kg$(mol_{Ln}h)^{-1}$).[13–16]

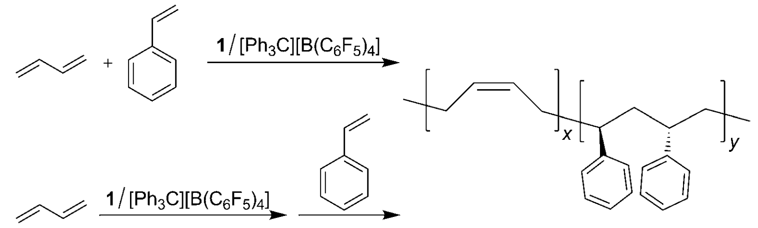
These copolymers were characterized by ^1H NMR spectroscopy to determine the styrene molar fraction (x_S) in the copolymers. As shown in Figure 2, the peaks appearing at $\delta = 6.52$–7.05 ppm were assigned to phenyl protons in the

Table 1. Syndiospecific homopolymerization of styrene (St) and cis-1,4-selective homopolymerization of butadiene (BD) catalyzed by 1/$[Ph_3C][B(C_6F_5)_4]$.[a]

Run	Monomer	[M]/[Ln]	*t* [min]	Conv. [%]	Activity[b]	*syn*-PS[c] [%]	*cis*-1,4[d] [%]	M_n[e] $\times10^{-4}$	M_w/M_n[e]	T_g[f] [°C]	T_m[f] [°C]
1	St	250	1	> 99	1560	> 99		5.3	1.97		270
2	St	500	1	> 99	3120	> 99		9.7	1.94		270
3	St	750	1	> 99	4680	> 99		15.3	1.98		271
4	St	1000	1	> 99	6240	> 99		22.3	1.88		270
5	BD	500	1	> 99	1620		97.1	3.1	1.24	−107	
6	BD	1000	1	> 99	3240		97.0	6.4	1.26	−106	
7	BD	2000	1	> 99	6480		97.0	13.2	1.25	−105	
8[g]	BD	1000	2	> 99	1620		97.1	6.3	1.28	−106	
9[h]	BD	500	10	70	114		99.0	3.6	2.13	−109	

[a] Polymerization conditions: Lu (10 μmol), [Lu]/[B] = 1:1 (mol/mol), toluene/monomer = 5:1 (v/v), $T_p = 20$ °C, unless otherwise noted. [b] Given in kg of polymer$(mol_{Lu}h)^{-1}$. [c] Measured by ^1H and ^{13}C NMR spectroscopy in $[D_4]$1,2-dichlorobenzene at 125 °C. [d] Determined by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ at 25 °C. [e] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard for *syn*-PS and in THF at 40 °C against polystyrene standard for PBD. [f] Determined by DSC. [g] After polymerization of 5 mmol of butadiene for 1 min, another 5 mmol of butadiene were added and the reaction mixture was stirred for another 1 min. [h] Chlorobenzene (5 mL).

Table 2. Butadiene (BD)–styrene (St) diblock copolymerization catalyzed by **1**/$[Ph_3C][B(C_6F_5)_4]$.[a]



Run	St fed [mol %]	*T* [min]	Conv. [%]	Activity[b]	St found[c] [mol %]	Microstructures[c] *cis*-1,4 [%]	*trans*-1,4 [%]	1,2 [%]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	T_g[e] [°C]	T_m[e] [°C]
1	10	10	86	306	4.7	95.5	2.8	1.7	8.8	1.43	−104	n.d.
2	20	10	81	312	12.7	95.3	2.7	2.0	10.4	1.41	−103	n.d.
3	40	10	77	342	29.1	95.2	3.0	1.8	11.5	1.29	−104	263
4	50	10	73	348	39.0	95.2	2.6	2.2	11.7	1.36	−105	264
5	60	10	67	336	46.4	95.3	3.1	1.8	12.1	1.34	−105	264
6	80	10	63	354	69.9	95.2	2.4	2.4	10.3	1.55	n.d.	265
7	90	10	67	396	85.4	95.1	2.4	2.5	9.8	1.68	n.d.	266
8[f]	50	5/5[g]	100/75	396	42.8	95.8	2.5	1.7	13.5	1.31	−105	268
9[h]	50	10/10[g]	100/46	306	31.5	95.7	2.4	1.9	22.5	1.39	−106	266

[a] Polymerization conditions: Lu (10 μmol), [Lu]/[B] = 1:1 (mol/mol), toluene (5 mL), [BD + St]/[Lu] = 1000:1 (mol/mol), $T_p = 20$ °C, unless otherwise noted. [b] Given in kg of copolymer $(mol_{Lu}\,h)^{-1}$. [c] Measured by ^1H and ^{13}C NMR spectra in $C_2D_2Cl_4$. [d] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard. [e] Determined by DSC. [f] Sequential copolymerization. Butadiene (5 mmol) was added first followed by styrene (5 mmol). [g] Sequential polymerization time. [h] Sequential copolymerization. Butadiene (10 mmol) was added first followed by styrene (10 mmol).

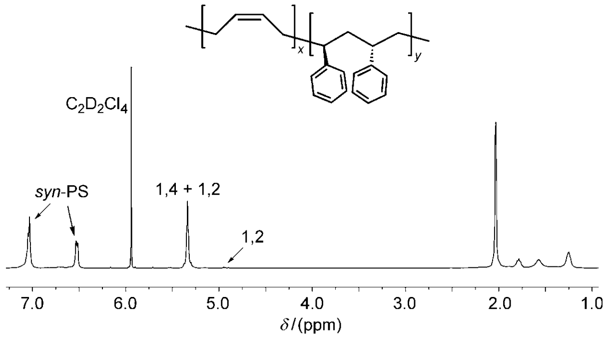


Figure 2. ^1H NMR spectrum ($C_2D_2Cl_4$) of diblock copolymer obtained by the concurrent addition of two monomers (Table 2, run 4, x_S = 39.0 mol %).

styrene units, whereas the peaks appearing at $\delta = 4.90$–5.34 ppm arose from the olefinic protons in the butadiene units. According to the intensity ratios of the phenyl and olefinic protons, it was found that the styrene molar fraction (x_S) in the copolymers varied correspondingly with the added molar fractions, reaching up to 85.4 mol % when its feed fraction was 90 mol %, which represents a rare example in which the copolymerization of St and BD provides a very high styrene incorporation.[13g] In addition, the results also suggest that the styrene content in the obtained butadiene–styrene copolymers could be facilely adjusted by changing the feeding ratios of monomers.

Gel permeation chromatography (GPC) analyses of these crude butadiene–styrene copolymers without extraction showed that the molecular weights were high ($M_n = 8.8$–12.1×10^4). Meanwhile, the molecular weight distributions were narrow and unimodal ($M_w/M_n = 1.29$–1.68), which is consistent with single-sited catalytic behavior and the formation of copolymers instead of a mixture of homopolymers (Figure 3a).

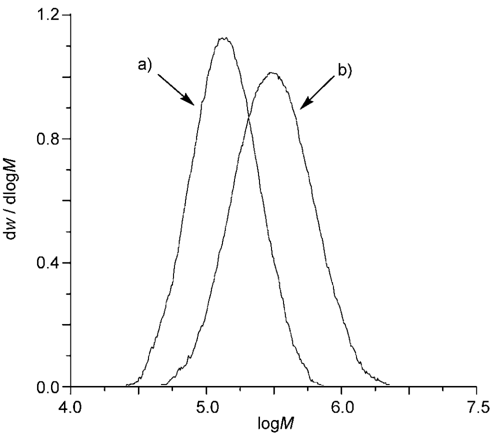


Figure 3. GPC curves of diblock copolymers obtained: a) by the concurrent addition of two monomers (Table 2, run 4) and b) by the sequential addition of two monomers (Table 2, run 9).

The microstructures of these copolymers were characterized by ^{13}C NMR spectroscopy analyses. The representative spectrum of a butadiene–styrene copolymer with a moderate styrene content of 39.0 mol % is provided in Figure 4a (Table 2, run 4). The strong and sharp singlets at $\delta = 145.13$ (*ipso*-Ph, *syn*-PS), 43.44 ($S_{\alpha\alpha}$, methylene), and 40.34 ppm ($T_{\beta\beta}$, methine), respectively, indicated that this copolymer contained a syndiotactic polystyrene block (*rrrr* > 99 %).[21] The sharp singlets observed at $\delta = 34.08$ (1,2-), 32.54 (*trans*-1,4), and 27.27 ppm (*cis*-1,4) were assignable to the PBD

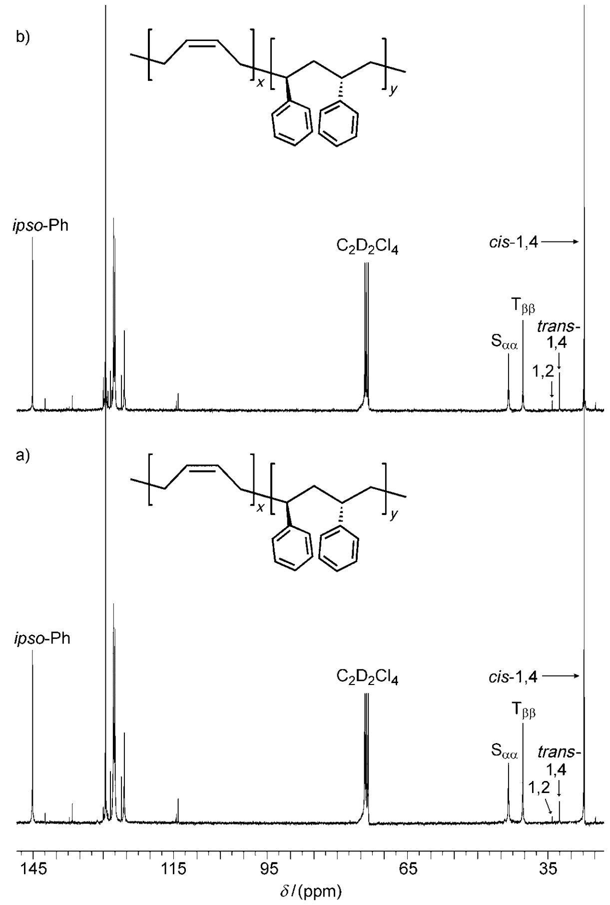


Figure 4. ^{13}C NMR spectra ($C_2D_2Cl_4$) of diblock copolymers obtained: a) by the concurrent addition of two monomers (Table 2, run 4, x_S = 39.0 mol %) and b) by the sequential addition of two monomers (Table 2, run 9, x_S = 31.5 mol %).

units in the copolymer.[22] Moreover, the very strong singlet at $\delta = 27.27$ ppm indicated an unambiguously high degree of *cis*-1,4-PBD units (>95 %).

Surprisingly to us, except for these resonances, those arising from the carbon–carbon linkages of the random butadiene–styrene segments reported in the literature were not observed ($\delta = 25$–50 ppm).[13–16] The ^{13}C NMR spectra of the other copolymers obtained with different styrene contents showed similar topologies. Meanwhile the *cis*-1,4 tacticity of the PBD segments remained unchanged (95.1–95.5 %) in all copolymers, which were not affected by varying the styrene content. This was in contrast to the previous reports that a high St incorporation rate caused a dramatic drop of the *cis*-1,4 tacticity of PBD units, as the insertion of butadiene into the styrene active species preferred *trans*-1,4 regularity. All these characterizations suggested that these copolymers obtained by using **1**/[Ph_3C][$B(C_6F_5)_4$] were different from those of random or multiblock styrene–butadiene copolymers obtained from any other catalyst system,[13c–d,f–h,14,16p] which might be butadiene–styrene diblock copolymers.

To confirm this deduction, a kinetics study of the copolymerization reaction in toluene at 20 °C by the concurrent addition of both monomers was carried out. As shown in Figure 5a, when the polymerization was carried out for 1 min, the isolated product was almost pure PBD according to its ^{1}H NMR spectrum (Figure 16 in the Supporting Information), which corresponds to the almost complete conversion (99 %) of butadiene, whereas no styrene incorporation was found. With the continuation of the polymerization and consumption of BD monomer, the styrene conversion in the copolymer increased drastically, whereas the butadiene conversion remained unchanged, which suggests that no more BD was incorporated into the copolymer once the active species was attached to the St monomer. Remarkably, PS units continued to propagate along with polymerization to reach up to 38.7 mol % PS units in the resultant product corresponding to 63.1 % conversion of St monomer (Figure 5b). These results indicated that even though it is in the presence of St, BD coordinated to the active metal center prior to the bulky St and remained inserted throughout. Only when BD was almost consumed, did St have an opportunity to insert into the Lu–PBD active species. As soon as the insertion was successful, St kept on propagating, leaving no chance for the very small amount of unreacted BD monomer. Therefore the diblock copolymer was isolated as the only product and no homopolymers were produced.

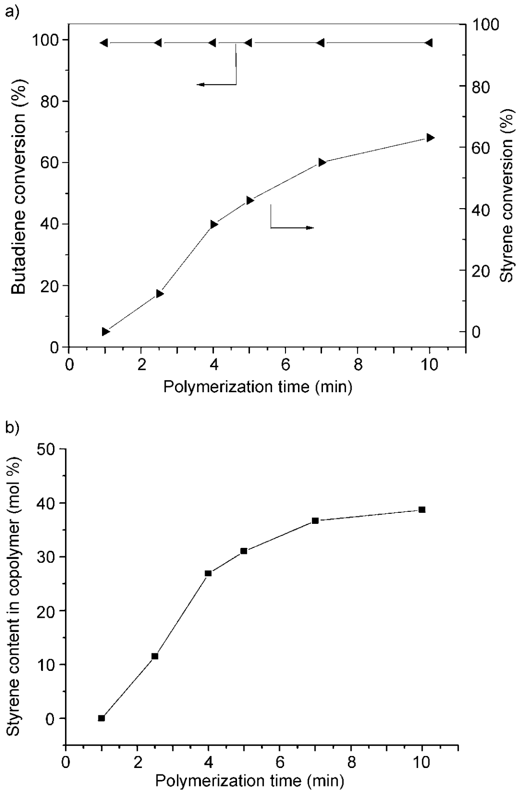


Figure 5. Kinetics curves (Table 2, run 4): a) conversion versus polymerization time, b) styrene content (x_S) in the copolymer versus polymerization time. Conditions: Lu (20 μmol), [Lu]/[B] = 1:1 (mol/mol), toluene (10 mL), [BD + St]/[Lu] = 1000:1 (mol/mol), [BD]/[St] = 1:1 (mol/mol), T_p = 20 °C.

For comparison, the copolymerization of butadiene and styrene by sequential addition of the two monomers was carried out under the same conditions (Table 2, runs 8 and 9). Upon addition of styrene to a polymerization system that gives 100 % conversion of butadiene, a butadiene–styrene diblock copolymer was obtained, selectively. As shown in Figure 3b, the narrow and unimodal curve of the molecular weight distributions confirmed the formation of pure diblock copolymers. If the addition sequence was reversed—namely, St was added first and polymerized to completeness, and then BD was added—we found that the GPC curve of the obtained polymer was bimodal, which suggests that the copolymer was not formed selectively. This further proved that BD insertion into the Lu–PSt active species was very difficult. The ^{13}C NMR spectrum (Figure 4b) of the obtained diblock copolymer (Table 2, run 9, $x_S = 31.5$ mol %) exhibited sharp singlets at $\delta = 145.16$ (*ipso*-Ph, *syn*-PS), 44.10 ($S_{\alpha\alpha}$, methylene), 40.87 ($T_{\beta\beta}$, methine), 34.18 (1,2-), 32.28 (*trans*-1,4), and 27.27 ppm (*cis*-1,4), demonstrating the presence of highly *cis*-1,4-regulated PBD blocks (95.7 %), which was unsurprisingly similar to the aforementioned copolymer (Figure 4a, Table 2, run 4, $x_S = 39.0$ mol %). These results solidly proved that the butadiene–styrene copolymers prepared by the concurrent addition of both monomers to the copolymerization reactions (Table 2, runs 1–7) were diblock copolymers.

The crystallinity of these copolymers was further investigated by DSC analysis. As shown in Table 2, no melting point was detected when the styrene content was lower than 12.7 mol % (Table 2, runs 1 and 2). Correspondingly, when the butadiene content in the copolymers was below 30.1 mol %, no glass transition temperature could be detected (Table 2, runs 6 and 7). In contrast, the samples of runs 3–7 in Table 2 showed high melting points (T_m) at 263–268 °C originating from the crystallizable *syn*-PS block, which were close to the value for the typical *syn*-PS homopolymer (≈ 270 °C). Correspondingly, the low T_g values of the copolymers (Table 2, runs 1–5) showed up around −107 to −103 °C originating from the high *cis*-1,4-PBD block, which were also comparable to those for the typical high *cis*-1,4 tactic PBD homopolymer (−109 °C, *cis*-1,4 > 99 %). It is noteworthy that the observed melting points (T_m) and glass transition temperature (T_g) remained unchanged as the styrene content in the copolymer samples increased, which further confirmed the diblock structure of these copolymers, namely, (*cis*-1,4-PBD)-*block*-(*syn*-PS).

All these butadiene–styrene diblock copolymers were further found to be completely insoluble in hexane, toluene, THF, or chloroform at room temperature within a week, except for those (runs 1 and 2) listed in Table 2 that dissolved in chloroform and THF within a week, owing to the low styrene content (< 12.7 mol %). These observations further corroborated the true copolymer nature of these polymers, whilst the existence of the crystalline *syn*-PS block in the obtained butadiene–styrene copolymers remarkably improved their chemical resistance in comparison with those of the SB or SBS materials prepared by anionic copolymerization. Moreover, the solvent-extraction experiments also demonstrated that the byproducts such as homopolybutadiene or atactic polystyrene were negligible in the copolymerization reactions.

Morphology of (*cis*-1,4-PBD)-*block*-(*syn*-PS) diblock copolymers: It is well known that the chemical, physical, and mechanical properties of *syn*-PS–PBD copolymers can be influenced by the crystalline form of the *syn*-PS component. It has been reported in the literature that *syn*-PS was observed in four crystalline forms, namely α, β, γ, and δ.[23] However, the polymorphic behavior of *syn*-PS became complicated by the fact that it is possible to produce clathrated forms when the α, γ, and δ crystalline forms are treated with either THF, halogenated, or aromatic solvents.[24] According to these reported results, we chose three representative diblock copolymer samples with different styrene contents (Table 2, runs 2, 7, and 9) for X-ray powder diffraction analysis (WXRD). As shown in Figure 6a, the X-ray powder profile of (*cis*-1,4-PBD)-*block*-(*syn*-PS) diblock copolymer, which has a low styrene molar fraction (Table 2, run 2, $x_S =$ 12.7 mol %), displays broad and very low intensity signals at $2\theta = 7.8$, 10.0, 17.4, 19.9, 23.1, and 28.1°, indicating a low crystallinity. This low crystallinity is very consistent with the observed result of the DSC curve, in which the endothermic peak of the crystalline block of *syn*-PS in the copolymer does not appear (Figure 11 in the Supporting Information). When the styrene content in the diblock copolymer increases to 85.4 mol % (Table 2, run 7), the WXRD spectrum exhibits strong reflections at $2\theta = 7.8$, 10.0, 17.4, 19.9, 23.1, and 28.1° (Figure 6b), which were assigned to the toluene δ

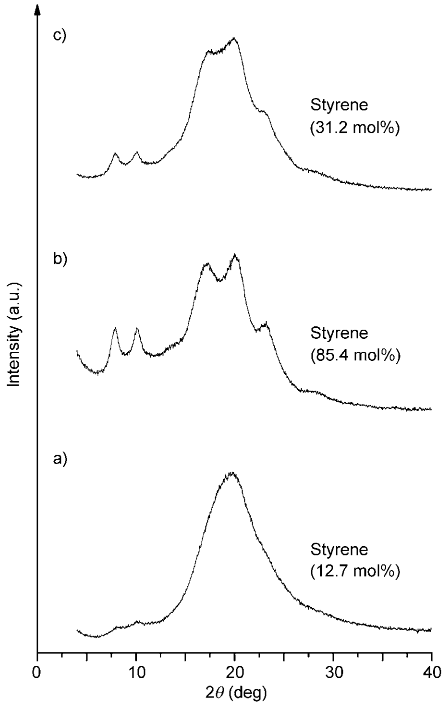


Figure 6. WAXD spectra of diblock copolymers obtained: a) Table 2, run 2, b) Table 2, run 7, by the concurrent addition of two monomers; and c) Table 2, run 9, by the sequential addition of two monomers.

clathrate crystalline form of *syn*-PS.[13c,f] Furthermore, we studied the WXRD of (*cis*-1,4-PBD)-*block*-(*syn*-PS) diblock copolymer with a moderate styrene content (Table 2, run 9, $x_S = 31.5$ mol%; Figure 6c). It displays similar signals to that of run 7, only with lower intensity than that of the sample with a higher styrene content. These results suggest that the crystallinity of these copolymers decreased with the decrease of styrene content in the copolymers.

To spread further light on the morphology and confirm the monomer distribution in the copolymers, one representative diblock copolymer sample with high styrene content (Table 2, run 7, $x_S = 85.4$ mol%) was analyzed by atomic force microscopy (AFM). As shown in Figure 7, the AFM micrographs of the sample indicate a remarkable phase-separated morphology of the hard and soft domains consisting of *syn*-PS and *cis*-1,4-PBD, respectively. This further demonstrates the block architecture of these copolymers.

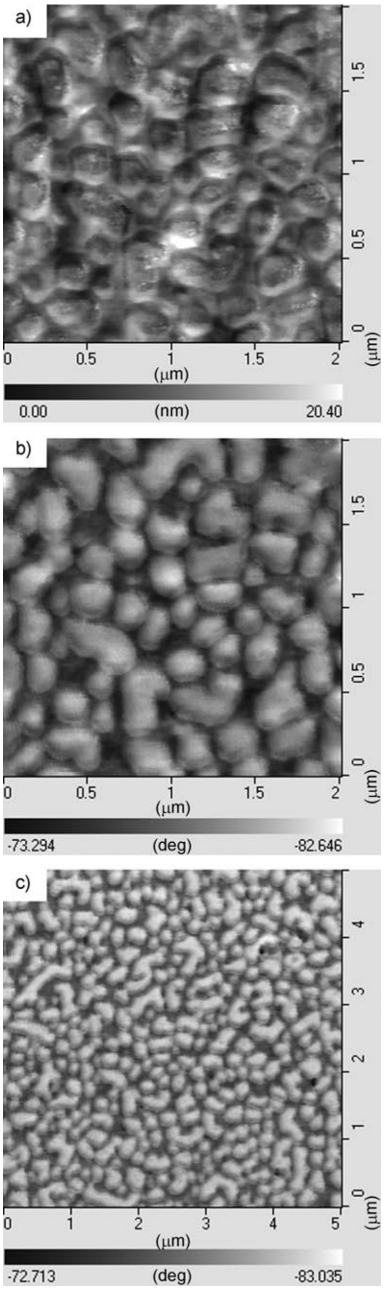


Figure 7. AFM micrographs of a spin-coated thin film of (*cis*-1,4-PBD)-*block*-(*syn*-PS) diblock copolymer obtained by the concurrent addition of two monomers (Table 2, run 7, $x_S = 84.5$ mol%): a) height image (scan size: 2 μm), b) phase image (scan size: 2 μm), and c) phase image (scan size: 5 μm).

Conclusion

We have reported the synthesis and full characterization of the novel linked-half-sandwich lutetium–bis(allyl) complex bearing an electron-withdrawing pyridyl-functionalized Cp ligand. Upon activation with $[Ph_3C][B(C_6F_5)_4]$, the complex shows excellent dual catalysis and outstanding activities for syndiotactic (*rrrr* > 99%) styrene polymerization, and for *cis*-1,4-selective butadiene polymerization (99%). More strikingly, a family of butadiene–styrene diblock copolymers, (*cis*-1,4-PBD)-*block*-(*syn*-PS), consisting of high *cis*-1,4 content (95%) of elastic PBD block and crystallizable *syn*-PS block (*rrrr* > 99%) were obtained for the first time through the concurrent or sequential addition of both monomers. The ^1H NMR spectrum analysis showed that these diblock copolymers covered the full range of styrene compositions ranging from 4.7 up to 85.4 mol%, which suggests that the block lengths of these diblock copolymers could be facilely controlled by changing the feeding ratios of monomers. The diblock structures of these obtained copolymers were fully corroborated by ^{13}C NMR spectroscopy, GPC analyses, kinetics investigation of the copolymerization, T_g and T_m analyses of DSC curves, chemical resistance experiments, and solvent extraction. X-ray powder diffraction analysis further showed that the crystallizable *syn*-PS block of these copolymers was in the toluene δ clathrate form and the crystallinity decreased with the decrease of the styrene content in the copolymers. Further studies on the mechanical aspect and the copolymerization of styrene with other monomers such as isoprene are in progress.

Experimental Section

General procedures and materials: All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified from an MBraun SPS system. Samples of the organo–rare-earth metal complex for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^1H and ^{13}C NMR spectra of the complex were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. Elemental analysis was performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Toluene was distilled from sodium/benzophenone under nitrogen and degassed thoroughly prior to use. Styrene (Aldrich) was dried over CaH_2 under stirring for 48 h and distilled under reduced pressure before use. Polymerization-grade 1,3-butadiene was dried by passing through a column filled with activated molecular sieves (4 Å) and then dissolved in toluene at −30 °C. [$Lu(\eta^3\text{-}C_3H_5)_3(diox)$] was prepared according to the literature.[17d] The ligand $C_5Me_4H{-}C_5H_4N$ was synthesized as described earlier.[25] [Ph_3C][$B(C_6F_5)_4$] was synthesized following the literature procedures.[26]

X-ray crystallographic studies: Crystals for X-ray analysis were obtained as described in the preparations below. The crystals were manipulated in a glovebox. Data collections were performed at −88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The determination of the crystal class and unit-cell parameters was carried out by the SMART program package.[27] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[28] The structures were solved by using the SHELXTL program.[29] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of complex 1: A solution of [$Lu(\eta^3\text{-}C_3H_5)_3(diox)$] (0.386 g, 1.0 mmol) in THF (10 mL) was treated at room temperature with a solution of ligand $C_5Me_4H{-}C_5H_4N$, (0.199 g, 1.0 mmol) in THF (5 mL). The resulting dark red solution was stirred for 30 min. The volume of solvent was reduced to 1 mL and toluene was added. After filtration, the dark red solution was stored at −30 °C. Complex **1** was isolated as orange-yellow crystals for several days (0.332 g, 73.0 %). ^{1}H NMR (400 MHz, [D_6]benzene, 25 °C): $\delta = 1.89$ (s, 6 H; $C_5\mathit{Me}_4$), 2.16 (s, 6 H; $C_5\mathit{Me}_4$), 3.10 (d, $^3J(H,H) = 12.4$ Hz, 8 H; $\mathit{CH}_2CH\mathit{CH}_2$), 6.33–6.46 (quintet, 2 H; $CH_2\mathit{CH}CH_2$), 6.53 (t, $^3J(H,H) = 12.0$ Hz, 1 H; $C_5\mathit{H}_4N$), 7.01–7.08 (m, 2 H; $C_5\mathit{H}_4N$), 7.92 ppm (d, $^3J(H,H) = 4.4$ Hz, 1 H; $C_5\mathit{H}_4N$); ^{13}C NMR (100 MHz, [D_6]benzene, 25 °C): $\delta = 11.80$ (s, 2 C; $C_5\mathit{Me}_4$), 11.99 (s, 2 C; $C_5\mathit{Me}_4$), 69.48 (s, 4 C; $\mathit{CH}_2CH\mathit{CH}_2$), 106.96 (s, 1 C; C_5Me_4), 118.02 (s, 2 C; C_5Me_4), 118.21(s, 2 C; C_5Me_4), 122.58 (s, 1 C; C_5H_4N), 126.17 (s, 1 C; C_5H_4N), 138.29 (s, 1 C; C_5H_4N), 149.70 (s, 2 C; $CH_2\mathit{CH}CH_2$), 150.58 (s, 1 C; C_5H_4N), 158.84 ppm (s, 1 C; *ipso*-C_5H_4N); element analysis calcd (%) for $C_{20}H_{26}NLu$: C 52.75, H 5.75, N 3.08; found: C 52.42, H 5.61, N 2.99.

Typical procedure for styrene homopolymerization: A typical polymerization reaction is given (Table 1, run 2): A solution of [Ph_3C][$B(C_6F_5)_4$] (9.2 mg, 10 μmol) in toluene (2 mL) was added to a solution of complex **1** (4.6 mg, 10 μmol) in toluene (1 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at room temperature for a few minutes, and styrene (0.52 g, 5 mmol) was added under vigorous stirring. The magnetic stirring was ceased within 1 min. The flask was then taken outside of the glove box. Methanol (2 mL) was added to terminate the polymerization. The mixture was poured into methanol (100 mL) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.52 g, 100 %).

Typical procedure for butadiene homopolymerization: A detailed polymerization procedure (Table 1, run 6) is described as a typical example: A solution of [Ph_3C][$B(C_6F_5)_4$] (9.2 mg, 10 μmol) in toluene (2 mL) was added to a solution of complex **1** (4.6 mg, 10 μmol) in toluene (1 mL) in a 25 mL flask under a nitrogen atmosphere. After a few minutes, butadiene (0.54 g, 10 mmol) was added and the reaction was carried out at 20 °C for 1 min to generate a viscous solution. The reaction was then terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The resulting polymer was poured into a large quantity of methanol and then dried under vacuum at room temperature to a constant weight (0.54 g, 100 %).

Typical procedure for butadiene and styrene copolymerization by the concurrent addition of both monomers: A typical copolymerization reaction is given (Table 2, run 4): A solution of [Ph_3C][$B(C_6F_5)_4$] (9.2 mg, 10 μmol) in toluene (2 mL) was added to a solution of complex **1** (4.6 mg, 10 μmol) in toluene (2 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at room temperature for a few minutes, and the mixture of styrene (0.52 g, 5 mmol) and butadiene (0.27 g, 5 mmol, 35 % butadiene in toluene) was added under vigorous stirring. The magnetic stirring was ceased within 2 min. The reaction was terminated after 10 min by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the copolymer product. The copolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (0.58 g, 73 %).

Typical procedure for butadiene and styrene copolymerization by the sequential addition of both monomers: A typical sequential copolymerization reaction is given as follows (Table 2, run 9): A solution of [Ph_3C][$B(C_6F_5)_4$] (9.2 mg, 10 μmol) in toluene (2 mL) was added to a solution of complex **1** (4.6 mg, 10 μmol) in toluene (2 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at room temperature for a few minutes, and butadiene (0.54 g, 10 mmol, 35 % butadiene in toluene) was firstly added under vigorous stirring. After 10 min of polymerization, styrene (1.04 g, 10 mmol) was then added to the polymerization solution. The copolymerization continuously proceeded for an additional 10 min and then was terminated by the addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent. The mixture was poured into methanol (200 mL) to precipitate the copolymer product. The copolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight (1.02 g, 64 %).

Characterization of polymers: The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polybutadiene were measured by a TOSOH HLC-8220 GPC with THF as eluent at 40 °C. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of syndiotactic polystyrene and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS columns at 150 °C. 1,2,4-Trichlorobenzene (TCB), containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol (BHT) was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration was made by using polystyrene standard Easi Cal PS-1 (PL Ltd). The ^{1}H and ^{13}C NMR spectra of polybutadiene were recorded on a Bruker AV600 (FT, 600 MHz for ^{1}H; 150 MHz for ^{13}C) spectrometer in $CDCl_3$ at 25 °C. The ^{1}H and ^{13}C NMR spectra of polystyrene were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer in [D_4]1,2-dichlorobenzene at 125 °C. The ^{1}H and ^{13}C NMR spectra of copolymers were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer in $C_2D_2Cl_4$. The T_g of polybutadiene and copolymers were measured through differential scanning calorimetry (DSC) analyses, which were carried out on a Perkin–Elmer Diamond differential scanning calorimeter at heating and cooling rates of 10 °C min^{-1} (temperature range: −140–150 °C). The T_m of polystyrene and copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC (TA Instruments) under a nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1} (temperature range: 50–300 °C). Wide-angle X-ray diffraction (WAXD) patterns of copolymer samples in the range $2\theta = 4$–40° were obtained with an automatic Philips instrument using the nickel-filtered $Cu_{K\alpha}$ radiation. AFM was used to study the surface topography of the spin-coated film. Images were obtained using a SPI3800N AFM (Seiko Instruments Inc., Japan) with a Si tip with a spring constant of 40 N m^{-1}. The cantilevers were operated slightly below their resonance frequency of around 200–400 kHz. The image acquisition was performed under ambient conditions. The AFM was used in tapping mode to reduce tip-induced surface degradation and sample damages. Imaging was conducted in the height and phase mode. Sample preparation: three drops (150 μL) of a 1.0 wt % solution in 1,1,2,2-tetrachloroethane of the copolymer were spin-coated on a glass surface for 15–20 s under ambient conditions at a speed of 1500 rpm. The sample was then analyzed by AFM after drying for a few days.

Crystal data of 1: $C_{20}H_{26}NLu$; $M_r = 455.39$; monoclinic; space group $P21/c$; $a = 8.4953(5)$, $b = 17.4871(10)$, $c = 12.5590(7)$ Å; $\alpha = 90°$, $\beta = 101.0300(10)°$, $\gamma = 90°$; $V = 1831.28(18)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.652$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 53.88$ cm^{-1}; 9950 reflections measured; 3252 reflections with $I_o > 2\sigma(I_o)$. Final $R1 = 0.0215$, $wR2 = 0.0535$ (all data).

CCDC-762575 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) N. Tomotsu, N. Ishihara, T. H. Newman, M. T. Malanga, *J. Mol. Catal. A* **1998**, *128*, 167; b) M. Malanga, *Adv. Mater.* **2000**, *12*, 1869.

[2] a) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464; b) N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* **1988**, *21*, 3356.

[3] a) J. Schellenberg, *Prog. Polym. Sci.* **2009**, *34*, 688; b) J. Schellenberg, H. J. Leder, *Adv. Polym. Technol.* **2006**, *25*, 141; c) J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* **2002**, *27*, 1925; d) A. S. Rodrigues, E. Kirillov, J. F. Carpentier, *Coord. Chem. Rev.* **2008**, *252*, 2115; e) C. Averbuj, E. Tish, M. S. Eisen, *J. Am. Chem. Soc.* **1998**, *120*, 8640; f) J. Okuda, E. Masoud, *Macromol. Chem. Phys.* **1998**, *199*, 543.

[4] E. Kirillov, C. W. Lehmann, A. Razavi, J. F. Carpentier, *J. Am. Chem. Soc.* **2004**, *126*, 12240.

[5] Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 13910.

[6] a) F. Jaroschik, T. Shima, X. Li, K. Mori, L. Ricard, X. F. Le Goff, F. Nief, Z. Hou, *Organometallics* **2007**, *26*, 5654; b) A. S. Rodrigues, E. Kirillov, C. W. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi, J. F. Carpentier, *Chem. Eur. J.* **2007**, *13*, 5548; c) M. Nishiura, T. Mashiko, Z. Hou, *Chem. Commun.* **2008**, 2019; d) X. Xu, Y. Cheng, J. Sun, *Chem. Eur. J.* **2009**, *15*, 846; e) F. Bonnet, C. D. C. Violante, P. Roussel, A. Mortreux, M. Visseaux, *Chem. Commun.* **2009**, 3380; f) X. Fang, X. Li, Z. Hou, J. Assoud, R. Zhao, *Organometallics* **2009**, *28*, 517.

[7] S. J. Quintavalla, S. H. Johnson, *Rubber Chem. Technol.* **2004**, *77*, 972.

[8] a) D. Wilson, *Makromol. Chem. Macromol. Symp.* **1993**, *66*, 273; b) E. Lauretti, B. Miani, F. Misttrali, *Rubber World* **1994**, *210*, 34.

[9] a) L. Friebe, O. Nuyken, W. Obrecht, *Adv. Polym. Sci.* **2006**, *204*, 1; b) A. Fischbach, R. Anwander, *Adv. Polym. Sci.* **2006**, *204*, 155; c) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404; d) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1; e) L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, *Angew. Chem.* **2008**, *120*, 2682; *Angew. Chem. Int. Ed.* **2008**, *47*, 2642; f) W. Gao, D. Cui, *J. Am. Chem. Soc.* **2008**, *130*, 4984, and references therein.

[10] A. Buonerba, C. Cuomo, V. Speranza, A. Grassi, *Macromolecules* **2010**, *43*, 367.

[11] J. N. Henderson, Styrene-Butadiene Rubbers, in *Rubber Technology*, 3rd ed., Chapman & Hall, London, **1995**, pp. 209.

[12] P. Wang, Y. Jin, F. Pei, F. Jing, Y. Sun, *Acta Polym. Sin.* **1994**, *4*, 392.

[13] a) C. Pellecchia, A. Proto, A. Zambelli, *Macromolecules* **1992**, *25*, 4450; b) A. Zambelli, P. Longo, P. Oliva, *Macromol. Chem. Phys.* **1994**, *195*, 2623; c) A. Grassi, M. Caprio, A. Zambelli, D. E. Bowen, *Macromolecules* **2000**, *33*, 8130; d) A. Zambelli, M. Caprio, A. Grassi, D. E. Bowen, *Macromol. Chem. Phys.* **2000**, *201*, 393; e) A. Zambelli, A. Grassi, M. Caprio, D. E. Bowen (The Goodyear Tire & Rubber Co.), Eur. Pat. Appl. EP 1013683, **2000**; f) M. Caprio, M. C. Serra, D. E. Bowen, A. Grassi, *Macromolecules* **2002**, *35*, 9315; g) S. Milione, C. Capacchione, C. Zannoni, A. Grassi, A. Proto, *Macromolecules* **2007**, *40*, 5638; h) C. Cuomo, M. C. Serra, M. G. Maupoey, A. Grassi, *Macromolecules* **2007**, *40*, 7089.

[14] N. Naga, Y. Imanishi, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 939.

[15] a) H. T. Ban, Y. Tsunogae, T. Shiono, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 2698; b) H. T. Ban, Y. Tsunogae, T. Shiono, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 1188; c) H. T. Ban, T. Kase, M. Kawabe, A. Miyazawa, T. Ishihara, H. Hagihara, Y. Tsunogae, T. Shiono, *Macromolecules* **2006**, *39*, 171.

[16] a) Y. Wu, G. Wu, Y. Qi, Y. Wei, *Syn. Rub. Ind.* **1992**, *15*, 154; b) E. Kobayashi, S. Kaita, S. Aoshima, J. Furukawa, *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 1195; c) A. Oehme, U. Gebauer, K. Gehrke, M. D. Lechner, *Macromol. Rapid Commun.* **1995**, *16*, 563; d) E. Kobayashi, S. Kaita, S. Aoshima, J. Furukawa, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2175; e) Y. Jin, P. Wang, F. Pei, G. Cheng, L. Cui, C. Song, *Polymer* **1996**, *37*, 349; f) E. Kobayashi, N. Hayashi, S. Aoshima, J. Furukawa, *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 241; g) E. Kobayashi, N. Hayashi, S. Aoshima, J. Furukawa, *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 1707; h) Q. Zhang, X. Ni, Y. Zhang, Z. Shen, *Macromol. Rapid Commun.* **2001**, *22*, 1493; i) S. Kaita, Z. Hou, Y. Wakatsuki, *Macromolecules* **2001**, *34*, 1539; j) Q. Zhang, X. Ni, Z. Shen, *Polym. Int.* **2002**, *51*, 208; k) Q. Zhang, W. Li, Z. Shen, *Eur. Polym. J.* **2002**, *38*, 869; l) V. Monteil, R. Spitz, C. Boisson, *Polym. Int.* **2004**, *53*, 576; m) Q. Zhang, X. Ni, Z. Shen, *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2004**, *41*, 39; n) H. Zhu, Y. Wu, J. Zhao, Q. Guo, Q. Huang, G. Wu, *J. Appl. Polym. Sci.* **2007**, *106*, 103; o) A. S. Rodrigues, E. Kirillov, B. Vuillemin, A. Razavi, J. F. Carpentier, *Polymer* **2008**, *49*, 2039; p) H. Zhang, Y. Luo, Z. Hou, *Macromolecules* **2008**, *41*, 1064.

[17] a) Z. Jian, D. Cui, Z. Hou, X. Li, *Chem. Commun.* **2010**, *46*, 3022; b) D. Robert, E. Abinet, T. Spaniol, J. Okuda, *Chem. Eur. J.* **2009**, *15*, 11937; c) N. Yu, M. Nishiura, X. Li, Z. Xi, Z. Hou, *Chem. Asian J.* **2008**, *3*, 1406; d) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Organometallics* **2005**, *24*, 3792; e) C. K. Simpson, R. E. White, C. N. Carlson, D. A. Wrobleski, C. J. Kuehl, T. A. Croce, I. M. Steele, B. L. Scott, V. G. Young, Jr., T. P. Hanusa, A. P. Sattelberger, K. D. John, *Organometallics* **2005**, *24*, 3685; f) S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **2002**, *203*, 1029; g) S. Maiwald, H. Weißenborn, C. Sommer, G. Müller, R. Taube, *J. Organomet. Chem.* **2001**, *640*, 1; h) R. Taube, S. Maiwald, J. Sieler, *J. Organomet. Chem.* **2001**, *621*, 327; i) S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **2001**, *202*, 1446; j) S. Maiwald, H. Weißenborn, H. Windisch, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **1997**, *198*, 3305.

[18] A. Rodrigues, E. Kirillov, T. Roisnel, A. Razavi, B. Vuillemin, J. F. Carpentier, *Angew. Chem.* **2007**, *119*, 7378; *Angew. Chem. Int. Ed.* **2007**, *46*, 7240.

[19] S. Bambirra, M. W. Bouwkamp, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **2004**, *126*, 9182.

[20] G. W. Coates, *Chem. Rev.* **2000**, *100*, 1223.

[21] A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, *Macromolecules* **1987**, *20*, 2035.

[22] S. Bywater, Y. Firat, P. E. Black, *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 669.

[23] G. Guerra, M. Vitagliano, C. DeRosa, V. Petraccone, P. Corradini, *Macromolecules* **1990**, *23*, 1539.

[24] a) A. Immirzi, F. DeCandia, P. Iannelli, V. Vittoria, A. Zambelli, *Makromol. Chem. Rapid Commun.* **1988**, *9*, 761; b) V. Vittoria, R. Russo, F. DeCandia, *Polymer* **1991**, *32*, 3371; c) C. DeRosa, M. Rapacciuolo, G. Guerra, V. Petraccone, P. Corradini, *Polymer* **1992**, *33*, 1423; d) Y. Chatani, Y. Shimane, Y. Inoue, T. Inagaki, T. Ishioka, T. Ijitsu, T. Yukinari, *Polymer* **1992**, *33*, 488; e) Y. Chatani, Y. Shimane, T. Inagaki, T. Ijitsu, T. Yukinari, H. Shikuma, *Polymer* **1993**, *34*, 1620; f) Y. Chatani, T. Inagaki, Y. Shimane, H. Shikuma, *Polymer* **1993**, *34*, 4841.

[25] U. Siemeling, V. Vorfeld, B. Neumann, H. G. Stammler, *Chem. Ber.* **1995**, *128*, 481.

[26] a) J. C. W. Chien, W. M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570; b) E. B. Tjaden, D. C. Swenson, R. F. Jordan, *Organometallics* **1995**, *14*, 371.

[27] Bruker, SMART version 5.054.

[28] SAINT and SADABS, version 6.22, Bruker AXS Inc., Madison, WI (USA), **2000**.

[29] G. M. Sheldrick, SHELXTL NT version 6.12, Bruker AXS Inc., Madison, WI (USA), **2000**.

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