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# Highly Syndioselective 3,4-*Trans* Polymerization of (*E*)-1-(4-Methylphenyl)-1,3-butadiene by Fluorenyl *N*-Heterocyclic Carbene Ligated Lutetium Bis(alkyl) Precursor

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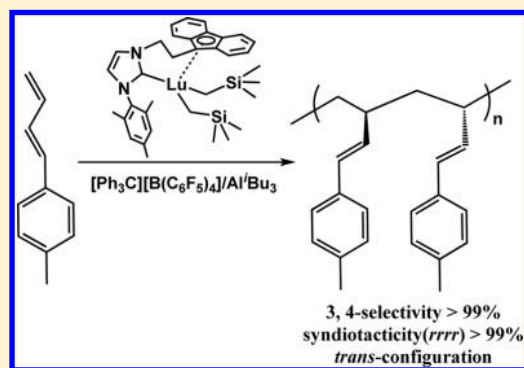
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## Supporting Information

**ABSTRACT:** (*E*)-1-(4-Methylphenyl)-1,3-butadiene (*E*-1-MPBD) synthesized via the “Wittig-type” reaction was polymerized with the ternary catalytic system (Flu-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>/Al<sup>*i*</sup>Bu<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Flu-NHC = C<sub>13</sub>H<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>(NCHCHN(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)C)) to afford a new product containing exclusively *trans*-3,4 (>99%) units with perfect syndiotacticity (*rrrr* > 99%). The regio-3,4 tacticity was proved by the IR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectroscopic analyses, while the 3,4-stereotacticity was confirmed by a model polymer with lower regularity (3,4 = 90.9%, *rrrr* = 49.3%) prepared by the binary catalytic system (Am-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Am-NHC = 2,6-<sup>*i*</sup>PrC<sub>6</sub>H<sub>3</sub>N=C(C<sub>6</sub>H<sub>5</sub>)-NCH<sub>2</sub>CH<sub>2</sub>(NCHCHN(C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6)C)). The *trans*-planar conformation was uncovered through 2D-NOESY and <sup>13</sup>C CPMAS NMR technologies. This represents the first stereo 3,4-syndioselective polymerization of 1,3-dienes achieved by a rare-earth metal based catalyst. Moreover, hydrogenating the resulting polymer gave the highly syndiotactic poly(4-methylphenyl-1-butene), which cannot be achieved by any other manner at the present stage.



## INTRODUCTION

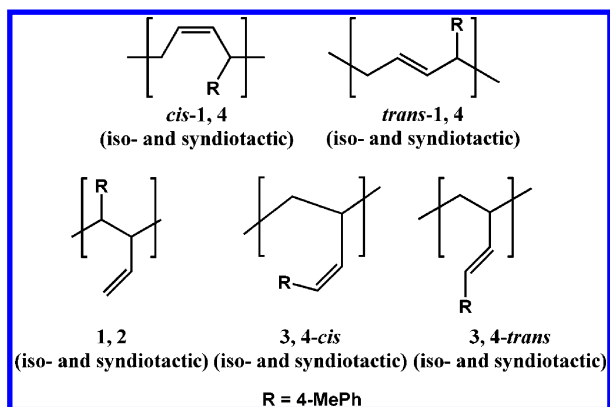
Polymers are one of the most intriguing materials of our modern world, able to assume a near-infinite variety of shapes and properties, which have permeated almost every aspect of our lives. The versatile properties and wide applications of polymer materials are closely related to the variable microstructures, the composition, and its distribution along the macromolecular chains, of which the tacticity is arguably the most critical one,<sup>1</sup> and how to control it has been a fascinating and challenging subject of polymer chemistry for decades. Polydienes as one subcategory of polyolefins exhibit more isomeric structures than poly- $\alpha$ -olefins because they involve more complicated regio- and stereotacticity,<sup>2</sup> having striking property discriminations. For example, *cis*-1,4-polyisoprene (PIP) is one of the most important rubbers,<sup>3</sup> *trans*-1,4-PIP is a plastics possessing shape memory function,<sup>4</sup> and 3,4-PIP is a very important component of high-performance rubbers because of its excellent wet-skid resistance and low rolling resistance,<sup>5</sup> and so on, while 1,2-polybutadienes with the stereoisotacticity or syndiotacticity can be used to prepare high-value-added fiber or long-life “green” tires.<sup>6</sup> Therefore, the substituted diene derivatives such as 1-phenyl-1,3-butadiene (1-PB) and 1-(4-methylphenyl)-1,3-butadiene (1-MPBD, *E* and *Z*

monomers) are anticipated to generate more diverse microstructured polymers; for instance, 1-MPBD can be polymerized theoretically into 10 kinds of stereoregular polymers (Chart 1) that are easier to be postfunctionalized. To date, 1-PB has been widely studied in cationic and anionic polymerization mechanisms for the past 50 years.<sup>7</sup> Masuda<sup>7a</sup> and Asami<sup>7b</sup> demonstrated that 1-PB could be polymerized via cationic catalysts such as stannic chloride, tungsten hexachloride, and triphenylmethylstannic pentachloride to afford P(1-PB) with more than 97% 3,4-units, whereas about half of the dangling double bonds were intramolecularly cyclized during the polymerization. Asami et al.<sup>7c</sup> reported that the anionic polymerization of 1-PB provided 95% *trans*-1,4 configuration. The only coordination polymerization of 1-PB was achieved by Longo et al.<sup>8</sup> with the Ni(acac)<sub>2</sub>/MAO or CpTiCl<sub>3</sub>/MAO system to give a 84% or 76% 3,4-selective polymer, respectively. In contrast, the polymerization of 1-MPBD possessing the similar reactivity to 1-PB has remained unexplored. Therefore, investigation of efficient coordination catalytic systems

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**Chart 1. Possible Stereoregular Polymers Obtainable from 1-MPBD**

providing regio- and stereoselectivity for the polymerization of 1-PB or 1-MPBD to afford polymers with designated microstructure, and absence of cyclization is an important research topic because the resultant stereoregular polydiene derivatives not only have different properties from their polydiene congeners but also can be hydrogenated across the double bonds to give various polyolefins such as poly(4-phenyl-1-butene) and alternating styrene–ethylene (S–E) copolymer, which cannot be obtained easily via other manners.<sup>9</sup>

Rare-earth metal complexes bearing cyclopentadienyl derivatives or noncyclopentadienyl ligands have achieved an upsurge in research interests, based on which the highly *cis*-1,4,<sup>3,10</sup> *trans*-1,4,<sup>4,11</sup> and 3,4-/1,2-<sup>5,12</sup> regio- and stereoisoselective polymerizations of butadiene/isoprene have been realized; however, the highly stereo-syndioselective 3,4-/1,2-polymerization has still remained an academic challenge for the rare-earth metal catalysts because the syndioselectivity needs a more sterically encumbered environment than the isoselectivity for the active metal centers, which is obviously difficult for the large rare-earth metal ions, and on the other hand, a steric bulky metal center takes a risk of losing activity. To date, the known catalysts for the highly 3,4-/1,2-syndioselective polymerizations of 1,3-dienes are all based on the small central metals such as Fe, Co, and Cr to meet the specific steric and electronic demanding of the *cis*- $\eta^4$ -coordination mode/C3 insertion of the monomers to the metal active species.<sup>13</sup> Herein we report the polymerization of (*E*)-1-MPBD with the cationic fluorenyl-modified *N*-heterocyclic carbene supported lutetium alkyl catalyst realizes for the first time the highly syndiotactic 3,4-*trans* triple selectivities. In addition, the hydrogenation of the isolated polymer to afford the highly syndiotactic poly(4-

methylphenyl-1-butene), a new type of polyolefin that cannot be obtained in any other manner, is also provided. The details of characterizing the microstructures and properties of these new polymers are discussed.

## RESULTS AND DISCUSSION

The Wittig reaction of phosphorus ylide and *trans*-4-methylcinnamaldehyde afforded (*E*)-1-MPBD in a high yield (89%) evidenced by giving the resonances at  $\delta$  5.18, 5.35, and 6.54 ppm assignable to the vinyl protons (the <sup>1</sup>H NMR spectrum, see Figure S1). (*E*)-1-MPBD was polymerized by the ternary catalytic system Flu-NHC-Lu/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al<sup>*i*</sup>Bu<sub>3</sub>, and the representative polymerization data are summarized in Table 1. The monomer conversion increased when the polymerization temperature changed from 25 °C (53.5%) to 50 °C (94.8%) but dropped slightly upon further elevating the temperature to 80 °C, probably due to the catalyst deactivation at high temperatures. Fixing the polymerization temperature at 50 °C, increasing gradually the monomer loading with the monomer-to-Lu ratio varying from 100:1 to 600:1 aroused the increase of the monomer conversion, suggesting the catalytic activity proportional to the monomer concentration. The activity of the present system was slightly lower than that recorded for the 3,4-isoprene polymerization with this or other catalyst systems,<sup>5,12</sup> which is in agreement with the steric bulkiness of the monomer 1-MPBD. Meanwhile the molecular weight of the resulting polymers showed almost linear correlation with the monomer-to-Lu ratio, and the molecular weight distribution was nearly constant, indicative of the single-sited catalytic system and the controllable polymerization fashion.

As polymerization of conjugated dienes involves the issue of regio- and stereoselectivities, thorough characterization of the microstructure of the resultant new product poly(1-MPBD) was mediated by IR and NMR spectroscopy measurements. The resonances at  $\delta$  6.50 and 6.05 ppm are attributed to the typical dangling olefinic protons CH=CH arising from the 3,4-units (Figure 1). The multiple signal at  $\delta$  2.70 and the triplet at 1.68 ppm (<sup>3</sup>J<sub>H–H</sub> = 6.0 Hz) are assigned to the methine and methylene protons CH<sub>2</sub>–CH in polymer main chains, respectively. No internal olefinic or aliphatic proton resonances of 1,4-units at  $\delta$  5.11, 5.30 ppm and  $\delta$  3.05, 3.39 ppm are found, indicating an over 99% 3,4-regioselectivity. In particular, the integral intensity ratio of the resonances for the phenyl, olefinic, and aliphatic protons is 4:2:3, meaning the absence of the cyclization, etc., side reactions in the polymerization process. The dangling double bonds can take *trans*- or *cis*- configuration. The olefin proton H<sub>1</sub> shows up as a doublet with a coupling

**Table 1. Polymerization of (*E*)-1-MPBD with Flu-NHC-Lu/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Al<sup>*i*</sup>Bu<sub>3</sub><sup>a</sup>**

entry	[( <i>E</i> )-1-MPBD]/[Lu]	temp (°C)	yield (%)	3,4- <sup>b</sup> (%)	rrrr (%) <sup>b</sup>	M <sub>n</sub> <sup>c</sup> × 10 <sup>−4</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>
1	200	25	53.5	>99	>99	2.1	1.6
2	200	50	94.8	99.0	>99	3.5	1.8
3	200	80	72.4	97.1	>99	2.4	2.1
4	100	50	65.6	98.8	>99	1.3	1.7
5	400	50	>99	98.5	>99	7.6	1.9
6	600	50	>99	98.6	96.0	9.7	1.9
7 <sup>d</sup>	200	50	52.1	90.9	49.3	3.9	1.5

<sup>a</sup>Conditions: Lu 10  $\mu$ mol, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] 10  $\mu$ mol, Al<sup>*i*</sup>Bu<sub>3</sub> 100  $\mu$ mol, toluene 3 mL, time 12 h. <sup>b</sup>Determined by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy in CDCl<sub>3</sub>. <sup>c</sup>Determined by GPC in THF at 40 °C against polystyrene standard. <sup>d</sup>(Am-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as catalyst.

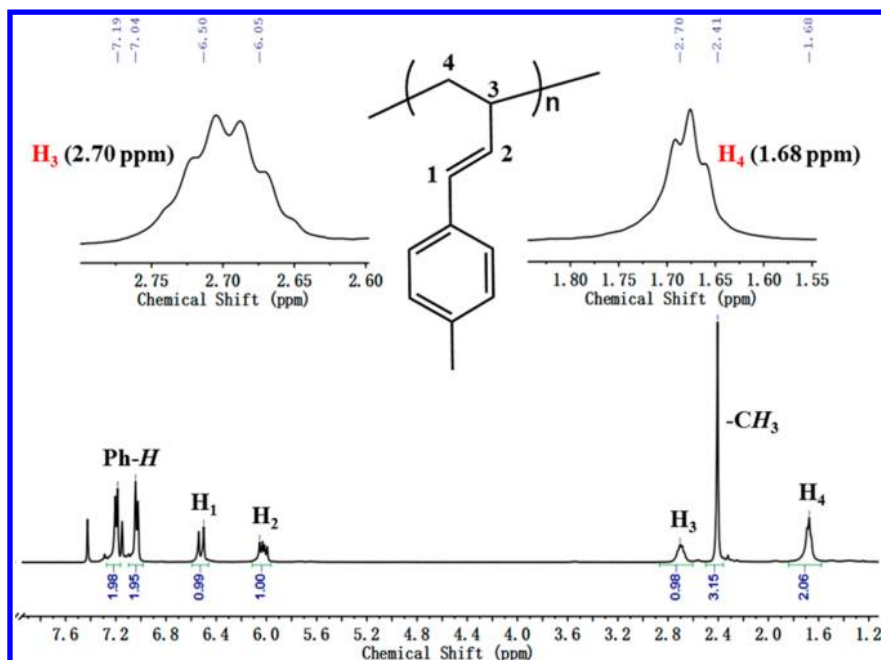


Figure 1.  $^1\text{H}$  NMR (120  $^\circ\text{C}$ ,  $o\text{-C}_6\text{D}_4\text{Cl}_2$ ) spectrum of poly(1-MPBD) (Table 1, entry 2).

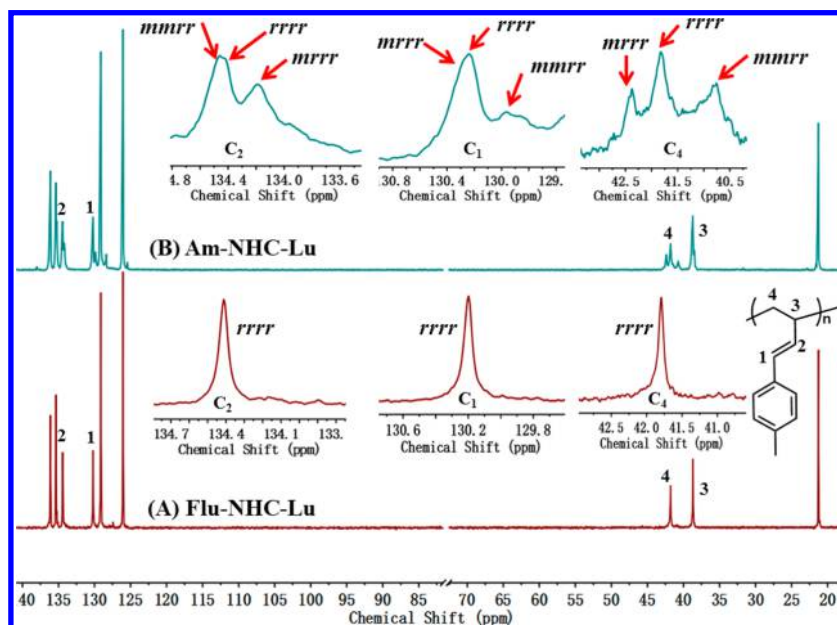


Figure 2.  $^{13}\text{C}$  NMR (25  $^\circ\text{C}$ ,  $\text{CDCl}_3$ ) spectra of poly(1-MPBD)s with Am-NHC-Lu (B) (Table 1, entry 7) and Flu-NHC-Lu (A) (Table 1, entry 2).

constant of  $^3J_{\text{CH}=\text{CH}} = 15.7 \text{ Hz}^{6c,14}$  relating to the *trans* configuration, in agreement with the strong absorption band at  $965 \text{ cm}^{-1}$  arising from the out-of-plane vibration of the *trans*-olefinic C–H bond in the IR spectrum (Figure S6).<sup>7c,d</sup> Note that the methylene protons display as a false triplet, meaning that the two protons set in the similar magnetic environment; thus, poly(1-MPBD) has the syndiotactic microstructure.<sup>15</sup> Correspondingly, all the olefinic carbons  $\text{C}_2$  and  $\text{C}_1$  and the methylene carbon  $\text{C}_4$  show strong and sharp singlets ( $^{13}\text{C}$  NMR spectrum, see Figure S7). These results were consistent with the identification of the syndiotactic polystyrene,<sup>16</sup> poly(methyl methacrylate),<sup>17</sup> 1,2-polybutadiene,<sup>18</sup> and 1,2-poly(pentadiene),<sup>2,14</sup> and the syndiotactically enriched ( $rr = 50\%$ ) polyisoprene prepared by this catalytic system.<sup>12a</sup>

To obtain a solid proof, a model sample with high 3,4-tacticity (90.9%) and low stereoregularity ( $rrrr = 49.3\%$ ) was synthesized by the polymerization of (*E*)-1-MPBD using the binary catalytic system (Am-NHC)Lu( $\text{CH}_2\text{SiMe}_3$ )<sub>2</sub>/[Ph<sub>3</sub>C][B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Table 1, entry 7).<sup>12c</sup> For comparison the  $^1\text{H}$  NMR spectra of two poly(1-MPBD)s obtained using the two different catalytic systems were combined in Figure S8. All the peaks of the stereoregular poly(1-MPBD) isolated from catalytic system Flu-NHC-Lu (Figure S8A) are sharp and clear while those from the less stereotactic poly(1-MPBD) obtained from the Am-NHC-Lu system are broad and more complicated (Figure S8B). In addition, the signals of the methylene protons from the former appear upfield at  $\delta$  1.22 ppm than that in the latter, in accordance with the *racemo* configuration.<sup>16</sup> The  $^{13}\text{C}$  NMR spectrum of the stereotactic poly(1-MPBD) gives three sharp

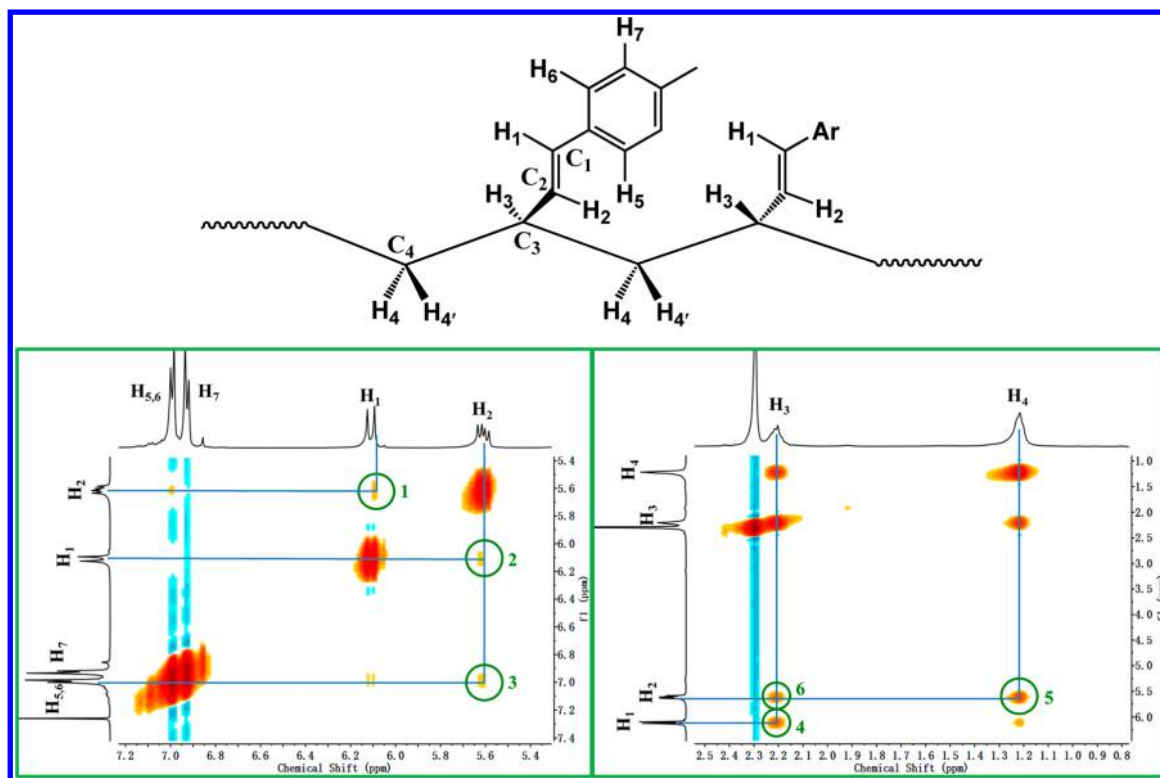
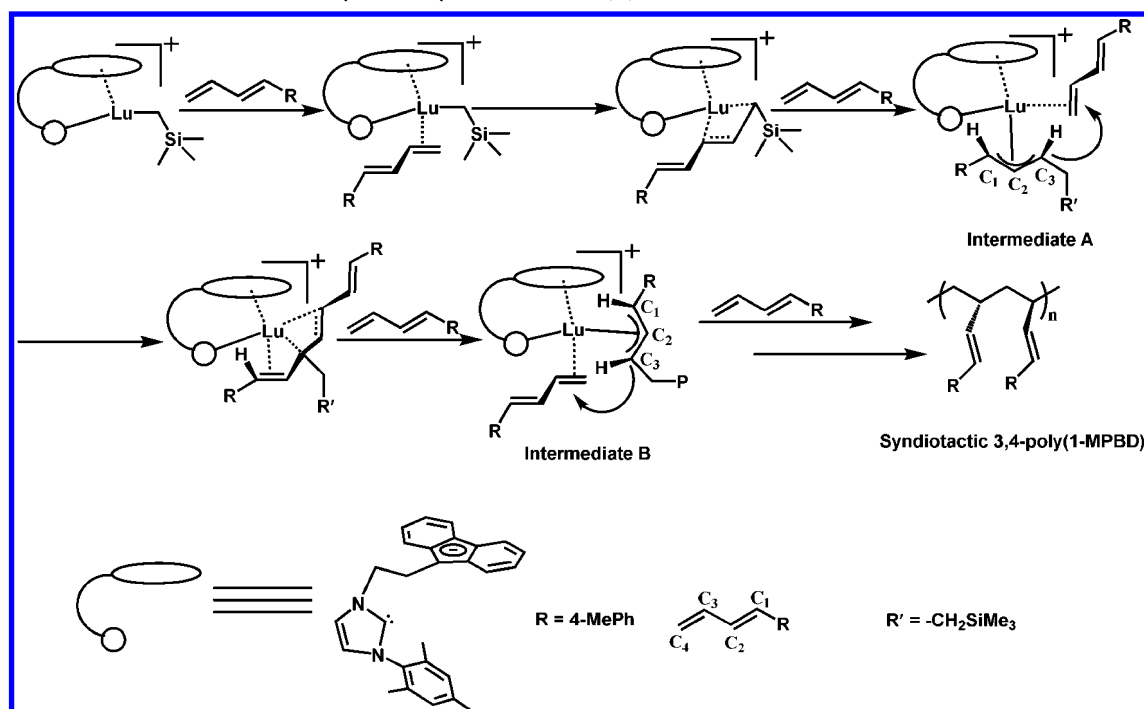


Figure 3. 2D-NOESY (25 °C, CDCl<sub>3</sub>) spectrum of poly(1-MPBD).

Scheme 1. Probable Mechanistic Pathway for Polymerization of (*E*)-1-MPBD

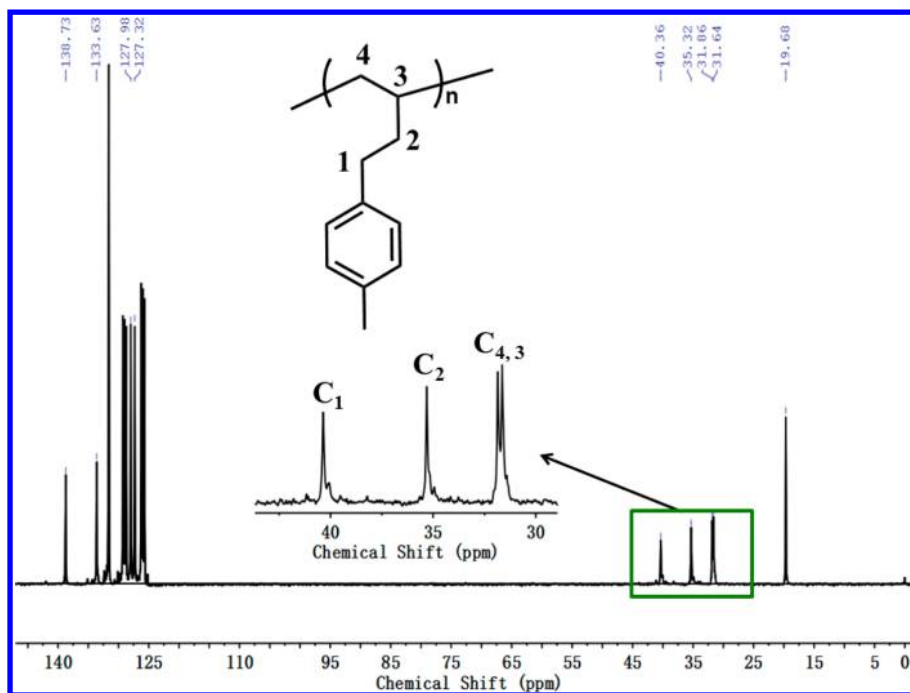


singlets at  $\delta$  134.41, 130.20, and 41.79 ppm assignable to the racemic pentad *rrrr* for C<sub>2</sub>, C<sub>1</sub>, and C<sub>4</sub>, respectively (Figure 2A). For the less stereotactic poly(1-MPBD), besides the racemic pentad *rrrr* resonances, there are also minor peaks at  $\delta$  134.50, 129.86, and 40.71 ppm attributed to the stereo errors of pentad *mmrr* (about 34.5%) and  $\delta$  134.21, 130.26, and 42.39 ppm of the pentad *mrrr* (about 16.2%) (Figure 2B).<sup>2,19</sup> Nevertheless, all of these peaks are not found at the same positions in Figure

2A, further attesting poly(1-MPBD) obtained with the catalytic system Flu-NHC-Lu is highly syndiotactic (*rrrr* > 99%).

**Conformation Analysis of Poly(1-MPBD).** The conformation of poly(1-MPBD) was investigated by using 2D-NOESY (two-dimensional nuclear Overhauser effect spectroscopy) equipment to measure the distance-dependent NOE effect between protons separated by less than 5 Å: the longer the distance between the protons, the weaker the interaction.<sup>20</sup>





**Figure 4.**  $^{13}\text{C}$  NMR (120  $^{\circ}\text{C}$ ,  $o\text{-C}_6\text{D}_4\text{Cl}_2$ ) spectrum of poly(4-MPBT).

As shown in Figure 3, the cross-peaks at positions 1 and 2 derived from protons  $\text{H}_1$  and  $\text{H}_2$  are weak, indicating a large spatial distance between them, alternatively, taking the *trans*-configuration. Protons  $\text{H}_2$  and  $\text{H}_5$  exhibit a weak cross-peak at position 3 probably owing to the rotation of the phenyl group disturbing the conjugation between the vinyl group and the phenyl ring. In particular, a strong cross-peak is observed at position 5, suggesting the group  $\text{H}_2\text{--C}_2\text{--C}_3\text{--C}_4\text{--H}_4$  is confined to the planar zigzag conformation. The similar two strong cross-peaks at positions 4 and 6 means the  $\text{C}_3\text{--H}_3$  bond adopting a *gauche* conformation to both the  $\text{C}_2\text{--H}_2$  bond and the  $\text{C}_1\text{=C}_2$  double bond. Both methylene  $\text{C}_4$  and methine  $\text{C}_3$  show as singlets ( $\delta$  41.96 ppm vs 39.63 ppm) in the  $^{13}\text{C}$  CPMAS (cross-polarization and magic-angle spinning, Figure S9) NMR spectrum, meaning each represents a type of chemically equivalent carbon. In particular, the one signal for the methylene  $\text{C}_4$  carbons may be arising from the *tttt* sequences, suggesting they are always *trans* to the methine  $\text{C}_3$  carbons in the  $\gamma$ -position.

The new polymer has a  $T_g$  of 90.6  $^{\circ}\text{C}$  close to that of polystyrene (Figure S10), probably possessing similar insulation and mechanical properties. Scanning the temperature range from 25 to 300  $^{\circ}\text{C}$ , no melting point was found, indicative of the amorphous morphology, which might be attributed to the dangling double bonds and the bulky substituents destroying the crystallinity of the macromolecular chains as displayed by the X-ray diffraction analysis (Figure S11).

**Probable Mechanism.** The coordination of 1,3-conjugated diene monomers to the transition metal ( $\text{M}_t$ ) active species adopts usually *cis*- and *trans*- $\eta^4$  and *cis*- and *trans*- $\eta^2$ , etc., eight modes. For the simple dienes such as butadiene, isoprene and (*E*)-pentadiene, the *cis*- $\eta^4$  coordination is the energetically most favored. Monomer (*E*)-1-MPBD in this work adopts the *trans*- $\eta^2$  coordination because of the bulky *para*-methyl phenyl substituent at  $\text{C}_1$ .<sup>8</sup> The probable mechanistic pathway is depicted as Scheme 1. The anionic attack of the Lu-alkyl active

species on the coordinating monomer forms the Lu- $\eta^3$ -allyl intermediate. The following insertion of the coordinating monomer into the Lu- $\eta^3$ -allyl moiety via  $\text{C}_4 \rightarrow \text{C}_1$  or  $\text{C}_4 \rightarrow \text{C}_3$  pathway gives correspondingly 1,4-unit or 3,4-unit, depending on the electronics and sterics of the monomer. The presence of a large substituent 4-MePh at  $\text{C}_1$  and its electron-donating property to  $\text{C}_3$  facilitate the latter one, leading to the 3,4-sequence. Nonetheless, if providing enough energy, the monomer can also take the *cis*- $\eta^4$  coordination, and the reaction occurs partially via  $\text{C}_4 \rightarrow \text{C}_1$ . This was proved by the fact that performing the polymerization at elevated temperature such as 80  $^{\circ}\text{C}$ , the *cis*-1,4 content increased to 2.9% (Table 1, entry 3). Meanwhile, owing to the restriction of the bulky CGC ligand, the monomer alternatively takes *si*-face and *re*-face with respect to the active metal center; therefore, the newly generated butenyl chain end adopts the opposite chirality to the penultimate one (Scheme 1, intermediates A and B), resulting in the 3,4-syndiotacticity. Changing the substituent at  $\text{C}_1$  gradually to smaller groups from Ph, and Me to H, the *cis*-1,4-unit in the products increases from 5.6% and 17.5% to 30.5% (Table S1), since the less encumbered monomer has more chance of taking *cis*- $\eta^4$  coordination mode, and the reactivity at  $\text{C}_1$  also increases. Overall, both the sterics and electronics of the ligand and the monomer are responsible for determining the stereochemistry of the polymer formed.

**Hydrogenation of Poly(1-MPBD).** Hydrogenation was carried out with *p*-toluenesulfonyl hydrazide (TSH) in refluxing *p*-xylene according to the literature.<sup>9</sup> The  $^1\text{H}$  NMR spectrum of the hydrogenated polymer poly(4-MPBT) shows that the signals arising from the olefinic protons at  $\delta$  6.50 and 6.05 ppm disappear completely, and the resonances at  $\delta$  2.53 and 1.34 ppm are assignable to the newly generated saturate ethylene group (Figure S12), suggesting the hydrogenation was successful. The  $^{13}\text{C}$  NMR spectrum (Figure 4) displays sharp singlets for all carbons, indicating the hydrogenated polymer still has a high tacticity. Comparing with the  $^{13}\text{C}$  NMR spectrum (Figure S13) of the isotactic enriched poly(4-PBT)

prepared by *rac*-Me<sub>2</sub>Si(2-MeBenz[e]Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO,<sup>21</sup> we found that the resonances of C<sub>2</sub> and C<sub>3</sub> at  $\delta$  35.32 and 31.64 ppm in poly(1-MPBD) shift upfield than those in poly(4-PBT), in correlation with the syndiotacticity.<sup>1</sup> This result demonstrated further poly(1-MPBD) had a high syndiotacticity that was not changed by hydrogenation.<sup>9</sup>

## CONCLUSIONS

We have demonstrated the highly syndiospecific 3,4-*trans* selective polymerization of (*E*)-1-(4-methylphenyl)-1,3-butadiene ((*E*)-1-MPBD) has been achieved for the first time by using the cationic NHC-ethylene fluorenyl lutetium alkyl precursor to give a new type of amorphous polymer with a high *T<sub>g</sub>* close to polystyrene. The 3,4-regio- and stereosyndiotacticity are well-defined by the combined IR and NMR spectroscopic analyses. Owing to this highly regio- and stereoregularity, the P(1-MPBD) macromolecular main chains take totally zigzag *trans* conformation in solution evidenced by NOESY and <sup>13</sup>C CPMAS spectra. Changing the substituent at C<sub>1</sub> of 1,3-butadiene from H, Me, Ph to 4-MePh, the resultant polymers have different content of the 3,4-units that increases with the volume of the substituent from 69.5, 82.5, 94.4 to 99%. These results allow us to deduce a probable reaction pathway for polymerization of (*E*)-1-MPBD:1-MPBD *trans*- $\eta^2$  coordinates to the cationic Lu<sup>3+</sup> center to form the Lu- $\eta^3$ -allyl intermediate, which attacks the monomer via C<sub>3</sub> at the C<sub>4</sub> of the monomer, generating a 3,4-linkage owing to the electronics of the *para*-methylphenyl electron-donating effect. The combined influences of the CGC-ligand and the bulky substituent of *para*-methylphenyl compel the alternating *si*-face and *re*-face coordination of the incoming monomer, which contributes to the highly syndiotacticity of the resultant polymer. In contrast to their syndiotactic polybutadiene analogue of crystalline plastic with a high melting point, this syndiotactic 3,4-P(1-MPBD) is an amorphous plastic, revealing that minimal changes in monomer structure arouses dramatically different properties. This work suggests the specific selective polymerization can be achieved by designing the electronically and sterically proper monomer, which might not be realized by the previously reported and widely employed design of catalytic precursors.

## EXPERIMENTAL SECTION

**General Methods and Materials.** All manipulations were performed under a dried and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in an Mbraun glovebox. All solvents were purified from Mbraun SPS system. Al<sup>i</sup>Bu<sub>3</sub> (1.0 M in hexane), *n*-butyllithium (1.6 M in hexane), allylmagnesium bromide (1.0 M in THF), 1,3-butadiene, and (*E*)-1,3-pentadiene were purchased from Aldrich. Benzyl chloride, *trans*-4-methylcinnamaldehyde, methyltriphenylphosphonium bromide, *trans*-cinnamaldehyde, and *p*-methylbenzenesulfonyl hydrazide (TSH) were purchased from the National Medicine Co. (China) and were used without further purification. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>22</sup> 4-phenyl-1-butene,<sup>21a</sup> (Flu-NHC)-Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>,<sup>22a</sup> and (Am-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub><sup>12c</sup> were prepared according to the literature. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 400 (FT, 400 MHz for <sup>1</sup>H; 100 MHz for <sup>13</sup>C). The number-average molecular weights (*M<sub>n</sub>*) and molecular weight distributions (*M<sub>w</sub>*/*M<sub>n</sub>*) of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOHLC-8220 GPC apparatus (column: SuperH2M-Hx3) at 40 °C using THF as the eluent (the flowing rate is 0.35 mL/min) against polystyrene standards or on a PL-GPC 220 type high-temperature chromatography equipped with three PL-gel 10  $\mu$ m Mixed-B LS type columns at 150 °C. The IR spectrum was recorded on a VERTEX 70 FT-IR

instrument. Differential scanning calorimetry (DSC) analyses were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku D/Max 2500 V PC X-ray diffractometer (Cu K $\alpha$ ,  $\lambda$  = 1.5406 Å).

**Synthesis of (*E*)-1-(4-Methylphenyl)-1,3-butadiene.** Under a nitrogen atmosphere, 75 mL of *n*-butyllithium (1.6 M in hexane, 0.12 mol) was added dropwise to a suspension of methyltriphenylphosphonium bromide (42.87 g, 0.12 mol) in 500 mL of dry THF within 30 min at -20 °C. After the mixture was stirred for 30 min, 100 mL of THF solution of 4-methylcinnamaldehyde (14.62 g, 0.10 mol) was added dropwise to the solution within 60 min. The mixture was stirred for another 2 h at -20 °C and then warmed to room temperature slowly and kept stirring overnight. After the mixture was poured into 500 mL of water and the organic phase was separated, the aqueous phase was extracted three times with diethyl ether (3  $\times$  100 mL). The combined organic phase were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. Flash chromatography (20% Et<sub>2</sub>O/hexane) afford the pure product in a yield of 89%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 7.26 ppm, 25 °C): 7.32 (d, 2H, Ar-H), 7.16 (d, 2H, Ar-H), 6.80–6.74 (m, 1H, olefin-H), 6.58–6.48 (m, 2H, olefin-H), 5.35 (d, 1H, olefin-H), 5.18 (d, 1H, olefin-H), 2.36 (s, 1H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 77.16 ppm, 25 °C): 137.66, 134.50, 129.47, 126.51, (m, 6C, Ar-C), 137.47, 132.97, 128.85, 117.14, (m, 4C, olefin-C) 21.37 (s, 1C, -CH<sub>3</sub>).

**Synthesis of Poly(1-MPBD).** A typical polymerization procedure (Table 1, entry 1) was described as follow. Under a nitrogen atmosphere, (*E*)-1-MPBD (0.288 g, 2 mmol) was added into a 10 mL flask. Then, 10 equiv of Al<sup>i</sup>Bu<sub>3</sub> (0.20 mL, 0.5 mol/L), a toluene solution (3.0 mL) of complex (Flu-NHC)Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (7.3 mg, 10  $\mu$ mol), and 1 equiv of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (9.2 mg, 10  $\mu$ mol) were added to the flask. The reaction apparatus was placed in a bath at 25 °C. After the reaction was stirred for 12 h, methanol was injected to terminate the polymerization. The viscous mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

**Synthesis of Syndiotactic Poly(4-methylphenyl-1-butene).** Under a nitrogen atmosphere, poly(1-MPBD) (0.404 g, 2.8 mmol of double bonds), *p*-toluenesulfonyl hydrazide (1.15 g, 6.2 mmol), and 50 mL of *p*-xylene were added to 100 mL flask and refluxed for 24 h. After being cooled to room temperature, the clear solution was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

**Synthesis of Isotactic Poly(4-phenyl-1-butene).** Under a nitrogen atmosphere, a toluene solution (4.0 mL) of complex *rac*-Me<sub>2</sub>Si(2-MeBenz[e]Ind)<sub>2</sub>ZrCl<sub>2</sub> (10 mg, 30  $\mu$ mol) and 300 equiv MAO were added into a 10 mL flask. The reaction apparatus was placed in a bath at 50 °C and stirred 5 min. Then, a toluene solution of 4-phenyl-1-butene (0.793 g, 6 mmol) was added into the flask. After the reaction was stirred for 4 h, methanol was carefully injected to terminate the polymerization. The mixture was poured into a large quantity of methanol. The obtained white polymer was filtered and then dried under vacuum at 40 °C to a constant weight.

## ASSOCIATED CONTENT

### Supporting Information

IR, <sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C CPMAS NMR spectra, WAXD pattern, and DSC thermogram of the selected polymer samples; table for the polymerization of butadiene, (*E*)-1,3-pentadiene, and (*E*)-1-phenyl-1,3-butadiene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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