

Highly 1,2-Selective Polymerization of 1,3-Butadiene with Rare-earth Metal Bis(alkyl)s Bearing an Iminophosphonamide Ligand

LIU Bo^{a,b}, LI Shihui^b, LI Danfeng^b, LV Kui^b, CUI Dongmei^{b,c*}, SUN Guangping^{a*}

(^aKey Laboratory of Automobile Materials of Ministry of Education, Department of Materials Science and Engineering, Jilin University, Changchun 130025, China;

^bState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China;

^cChangzhou Institute of Energy Storage Materials & Devices, Changzhou 213022)

Abstract Treatment of scandium tris(alkyl)s, $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$, with 2-Me-C₆H₄NHPPH₂=NC₆H₂-2,4,6-Me₃(NPN^{Ar}H) via deprotonation affords the bis(alkyl) derivative $[\text{NPN}^{\text{Ar}}]\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$. The complex structure was characterized by means of ¹H NMR, ¹³C NMR, elemental analysis and X-ray diffraction analysis. Complex activated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Al*i*Bu₃ exhibited highly catalytic activity to the polymerization of butadiene. The 1,2-selectivity of polybutadiene noticeably increased with decrease of temperature. The molecular mass is 2.95×10^4 and the molecular mass distribution (M_w/M_n) is 1.65 at -75 °C.

Keywords butadiene, selectivity, catalytic activity

CLC number: O632

Document code: A

Article ID: 1000-0518(2012)12-1394-05

DOI: 10.3724/SP.J.1095.2012.20431

The preparation of polydienes with designated microstructures and properties by controlling the regio- and stereoselectivity of dienes polymerization has been a fascinating and challenging research field, because of their widely demanding from the synthetic elastomer industry^[1]. For this goal, various catalyst systems providing regio- and stereoselectivity for the polymerization of dienes have been reported^[2-11]. However, only few catalytic systems can initiate the 1,2-polymerization of butadiene, as butadiene prefers to coordinate to the metal center of many catalytic systems in a *cis*-1,4 mode, generating a thermally stable η^3 - π -butenyl species, whereas coordinating in a 1,2- η^2 -mode to leave the vinyl group dangling, the steric hindrance at the metal center is requisite. To date, the efficient 1,2-selective systems have been mainly limited to the patented organolithium^[12], and transition metal initiator systems such as AlEt₃-Ti(OR)₄, (η^3 -C₃H₅)₃Cr, (η^3 -C₈H₁₃)(C₄H₆)Co, Mo(η^3 -C₃H₅)₄-CH₂=CHCH₂I, and Nb(η^3 -C₃H₅)₃, etc^[13]. Although, rare-earth metal complexes have exerted distinguished performances in the *cis*- and *trans*-1,4 selective polymerization of the conjugated dienes^[2,5-10], they have not shown 1,2-selectivity for 1,3-butadiene. Therefore, further exploration of new catalyst systems based on rare-earth metals and other elements is obviously challenging and attractive.

Herein, we report that NPN^{Ar}-type scandium bis(alkyl) complex activated by aluminum alkyls and borate initiates the polymerization of butadiene with high 1,2-selectivity. The content of 1,2-units of polybutadiene was found to be highly dependent on the reaction temperature, *i. e.*, the lower the polymerization temperature is, the higher the content of 1,2-units is. As far as we are aware, this is the first example of high 1,2-

Received: 2012-09-27, Revised: 2012-10-18

Correspondent: CUI Dongmei, professor; Tel: 0431-85262774; Fax: 0431-85262773; E-mail: dmcul@ciac.jl.cn; Research Interests: polymer physics and chemistry

Co-correspondent: SUN Guangping, professor; Tel: 0431-85095170; E-mail: sungp@jlu.edu.cn; Research Interests: polymer chemistry

selectivity polymerization of butadiene initiated by the cationic initiator system.

1 Experiment

1.1 Materials and Measurements

All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high vacuum Schlenk techniques or in a glove box. All solvents were purified from MBRAUN SPS system. mesityl azide, 2-Me-C₆H₄NHPPH₂(**1**), [Ph₃C][B(C₆F₅)₄] and Sc(CH₂SiMe₃)₃(THF)₂ were prepared according to published procedures^[14]. Butadiene (> 99%) was dried by passing through a Dryclean column (4A molecule sieves) and the toluene solution of AlEt₃. ¹H NMR, ¹³C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ¹H NMR; 100 MHz for ¹³C NMR) or AV300 (FT, 300 MHz for ¹H NMR; 75 MHz for ¹³C NMR). NMR assignments were confirmed by the ¹H-¹H (COSY), ¹H-¹³C (HMQC) experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). The molecular mass (*M_n*) were measured by TOSOH HLC-8220 GPC at 40 °C using THF as the eluent (the flowing rate was 0.35 mL/min) against polystyrene standards.

1.2 Synthesis of 2-Me-C₆H₄NHPPH₂=NC₆H₂-2,4,6-Me₃ (**2**, NPN^{Ar}H)

In a 100 mL Schlenk flask, a THF solution (15 mL) of mesityl azide (6.1 mmol, 0.97 g) was added dropwise to a THF solution (30 mL) of 2-methylanilindiphenylphosphine(**1**), (6.0 mmol, 1.74 g) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature. Removal of volatiles gave white solids that were further purified by washing with diethyl ether/hexane to afford pure white solids of NPN^{Ar}H (1.78 g, 70% yield). ¹H NMR (300 MHz, CDCl₃, 25 °C), δ: 2.00 (d, *J*_{P-H} = 0.7 Hz, 6H, *o*-NC₆H₂Me₃), 2.13 (d, *J*_{P-H} = 2.2 Hz, 3H, *p*-NC₆H₂Me₃), 2.18 (s, 3H, C₆H₄Me), 5.07 (b, 1H, NH), 6.67 (s, 2H, NC₆H₂), 6.72 (t, *J*_{H-H} = 7.2 Hz, 1H, 4-NC₆H₄), 6.84 (t, *J*_{H-H} = 7.2 Hz, 1H, 5-NC₆H₄), 7.06 (d, *J*_{H-H} = 7.2 Hz, 1H, 3-NC₆H₄), 7.32 ~ 7.38 (m, 4H, *m*-PC₆H₅), 7.41 ~ 7.46 (m, 2H, *p*-PC₆H₅), 7.71 ~ 7.78 (m, 4H, *o*-PC₆H₅). ¹³C NMR (75 MHz, C₆D₆, 25 °C), δ: 18.16 (s, 1C, C₆H₄Me), 20.66 (s, 2C, *o*-NC₆H₂Me₃), 21.03 (s, 1C, *p*-NC₆H₂Me₃), 118.46 (aryl), 121.38 (aryl), 124.73 (aryl), 127.16 (aryl), 128.24 (aryl), 128.95 (aryl), 129.08 (aryl), 129.25 (aryl), 130.79 (aryl), 132.04 (aryl), 132.28 (aryl), 132.40 (aryl), 133.67 (aryl), 140.06 (aryl), 143.89 (aryl). Element anal. calcd (%) for C₂₈H₂₉N₂P: C 79.22, H 6.89, N 6.60, found: C 79.12, H 6.92, N 6.63.

1.3 Synthesis of (NPN)Sc(CH₂SiMe₃)₂(THF)(**3**)

To a hexane solution (2.0 mL) of Sc(CH₂SiMe₃)₃(THF)₂ (0.180 g, 0.4 mmol), an equivalent of compound **2** (0.170 g, 0.4 mmol in 3 mL THF) was dropwise added at the room temperature. The mixture remained stirring for 30 min at the room temperature and then was concentrated to about 0.5 mL. Addition of 2 mL hexane and cooling to -30 °C for 2 days afforded crystalline solids that were washed with a small amount of hexane to remove impurities and dried in vacuo to give pale yellow powders of complex **3** (0.17 g, 59% yield). ¹H NMR (400 MHz, C₆D₆, 25 °C), δ: 0.45 (m, 22H, CH₂SiMe₃), 1.14 (br, 4H, THF), 1.81 (d, *J*_{P-H} = 1.2 Hz, 6H, *o*-NC₆H₂Me₃), 2.19 (d, *J*_{P-H} = 2.4 Hz, 3H, *p*-NC₆H₂Me₃), 3.39 (s, 3H, C₆H₄Me), 3.86 (br, 4H, THF), 6.68 (d, *J*_{H-H} = 7.6 Hz, 6-NC₆H₄Me), 6.71 (s, 2H, NC₆H₂), 6.78 ~ 6.85 (m, 2H, 4,5-NC₆H₄Me), 6.98 ~ 7.03 (m, 4H, *m*-PC₆H₅), 7.05 ~ 7.13 (m, 2H, *p*-PC₆H₅), 7.35 (d, 3*J*_{H-H} = 6.8 Hz, 1H, 3-NC₆H₄Me), 7.69 ~ 7.74 (m, 4H, *o*-PC₆H₅). ¹³C NMR (100 MHz, C₆D₆, 25 °C), δ: 4.76 (s, 6C, SiMe₃), 21.14 (s, 3C, NC₆H₂Me₃), 23.85 (s, 1C, NC₆H₄Me), 25.53 (s, 2C, THF), 42.14 (br, 2C, CH₂SiMe₃), 70.80 (s, 2C, THF), 121.14 (s, 1C, *p*-NC₆H₄Me), 123.40 (d, 3*J*_{P-C} = 10 Hz, 2C, 6-NC₆H₄Me), 126.48 (s, 1C, 5-NC₆H₄Me), 128.93 (d, 3*J*_{P-C} = 11 Hz, 4C, *m*-PC₆H₅), 129.78 (s, 1C, *p*-NC₆H₂), 129.93 (s, 2C, *m*-NC₆H₂),

131. 83 (s, 1C, ipso-MeC₆H₄), 131. 99 (s, 2C, *p*-PC₆H₅), 133. 26 (d, 4C, *o*-PC₆H₅), 135. 59 (d, 1J_{p-c} = 5 Hz, 2C, ipso-PC₆H₅), 141. 92 (s, 1C, ipso-NC₆H₂), 148. 41 (s, 1C, ipso-NC₆H₄). Elemental anal. calcd (%) for C₄₀H₅₈N₂OPSi₂Sc:C 71. 70, H 8. 72, N 4. 18, found: C 71. 65, H 8. 79, N 4. 21.

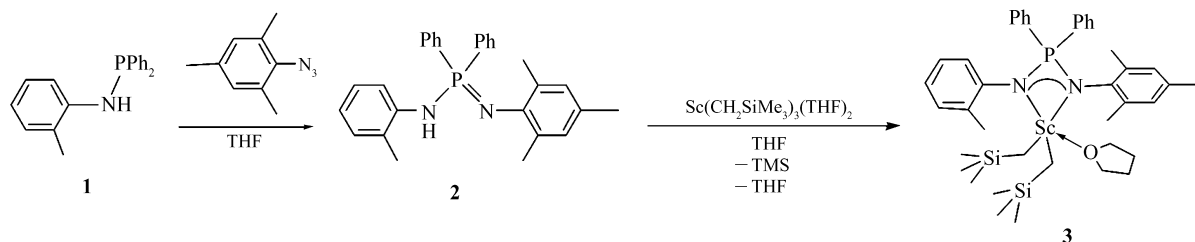
1.4 Butadiene Polymerization

A typical polymerization procedure was described as follow. Butadiene, [Ph₃C][B(C₆F₅)₄], Al₃IBu₃ and 20 mL toluene were charged into a flask. After 15 min, the viscous reaction solution was poured into ethanol (ca. 40 mL) containing a small amount of hydrochloric acid to terminate the polymerization. The white solids of polymer was precipitated, filtered, washed with ethanol, and dried under vacuum at 30 °C to a constant mass.

2 Results and Discussion

2.1 Structure of (NPN)Sc(CH₂SiMe₃)₂(THF)(3)

Staudinger reaction between aminodiphenylphosphine ArNHPPH₂ (**1**) and 1 equiv of mesityl azide afforded iminophosphonamine compound ArNHP(Ph₂)=NC₆H₂Me₃-2,4,6 (2 (NPN^{Ar}H), Ar = 2-Me-C₆H₄). Treatment of scandium tris(alkyl)s, Sc(CH₂SiMe₃)₃(THF)₂, with compound **2** via deprotonation produced the bis(alkyl) derivative [NPN^{Ar}]Sc(CH₂SiMe₃)₂(THF)(**3**) in 70% isolated yield (Scheme 1). The



Scheme 1 Synthesis of complex **3**

colorless crystals of complex **3** grew from a mixture of THF/hexane at -30 °C in 2 d. The molecular structure of complex **3** was confirmed by X-ray diffraction analysis as a monomer with a solvated THF molecule, adopting a distorted tetrahedron geometry around the metal center (Fig. 1). The two alkyl species are located in *cis*-positions. The NPN^{Ar} ligand chelates to the metal ion in a η^2 -meridional configuration, leading to the two *N*-aryl rings mode to generate perpendicular to each other. This structure is strongly reminiscent of complex [NPN^{Ph}]Sc(CH₂SiMe₃)₂(THF)^[12] reported previously, whereas the bond distances and angles formed by Sc and the chelating atoms in complex **3** are longer or larger, respectively, in response to the more sterics of the NPN^{Ar} as compared with NPN^{Ph} in the latter complex. For instance, the average Sc—N bond length of 0. 2227(8) nm and the Sc(1)—P(1) bond length of 0. 2884(3) nm in complex **3** are longer than 0. 2189(3) nm for Sc—N and 0. 2874(3) nm for Sc—P in [NPN^{Ph}]Sc(CH₂SiMe₃)₂(THF)^[11]; and

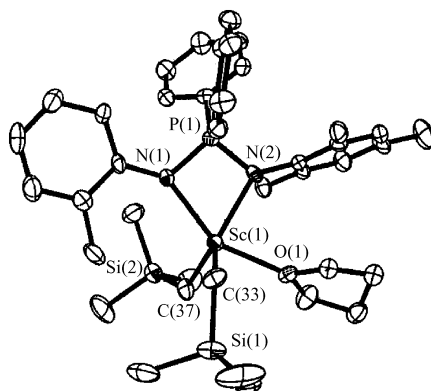


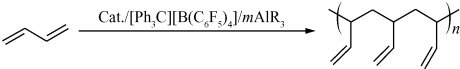
Fig. 1 Molecular structure of complex **3** (hydrogen atoms omitted for clarity, unlabeled atoms are carbons) Selected bond lengths (nm) and angles (°): Sc(1)—N(1) 0. 2251(8), Sc(1)—N(2) 0. 2202(7), Sc(1)—O(1) 0. 2222(7), Sc(1)—C(33) 0. 2231(10), Sc(1)—C(37) 0. 2258(11), Sc(1)—P(1) 0. 2884(3), N(1)—P(1) 0. 1631(8), N(2)—P(1) 0. 1571(8); N(2)—Sc(1)—N(1) 66. 9(3), C(33)—Sc(1)—C(37) 113. 6(4), O(1)—Sc(1)—C(33) 87. 7(3), O(1)—Sc(1)—C(37) 91. 1(3)

the bond angles of CH₂—Sc—CH₂ (113. 6(4)°) and N(2)—Sc(1)—N(1) angle (66. 9(3)°) in complex **3** are larger than the related 111. 90(12)° and 64. 56(9)°.

2.2 Butadiene Polymerization

Complex **3** was activated with [Ph₃C][B(C₆F₅)₄] to generate cationic unit that could not catalyze the polymerization of butadiene. This might be ascribed to the impurities in the polymerization solution or the unstable nature of the cationic unit that decomposed into nonactive species. Addition of a slight excess of Al*i*Bu₃, the cationic unit exhibited highly catalytic activity to the polymerization of butadiene (Table 1, run 2). Unfortunately, the resultant polybutadiene(PB) was gelled and only partially soluble in chloroform. By decreasing the polymerization temperature to −20 °C, the resultant PB was soluble in CHCl₃, whereas the GPC curve of the product became bimodal (Table 1, run 3). This result indicated that the molecular chains of 1,2-regulated PB were still partially crosslinked although without formation of gel. When the polymerization temperature was decreased further to −40 °C, the crosslinking of the polymer chains was efficiently inhibited and the bimodal problem observed above was also solved successfully, although the catalytic activity became lower at this condition (Table 1, run 4). The 1,2-regularity of PB obtained noticeably increased with decrease of temperature (Table 1, runs 2 ~ 6), which reached strikingly up to 98. 0% in a reasonable yield when the polymerization was carried out at −75 °C, meanwhile the molecular mass increase greatly to 2. 95 × 10⁴ whilst the molecular mass distribution kept at a narrow range (*M_w*/*M_n* = 1. 64), which could be ascribed to the restrained chain tranfer. The influence of monomer-to-initiator ratio also was investigated. The molecular mass of the resultant PB increased with the ratio whilst the 1,2-regularity as well as the molecular mass distribution did not change (Table 1, runs 6,7). To the best of our knowledge, this is the first highly 1,2-selective cationic catalyst system based on rare-earth metal complexes for the polymerization of butadiene as far as we were aware.

Table 1 Polymerization of butadiene by complex 3^a



Run	[Al]/[Sc]	Temperature/°C	Time/h	Yield/%	Microstructures ^b			10 ^{−4} <i>M</i> _n ^c	<i>M_w</i> / <i>M_n</i>
					1, 2-	1, 4- <i>trans</i>	1, 4- <i>cis</i>		
1	0	25	1	—	—	—	—	—	—
2	10	25	1	87	13. 2	—	—	—	—
3	40	−20	4	28	62. 1	2. 1	35. 8	0. 24:2. 35	1. 47:1. 09
4	40	−40	14	45	79. 3	1. 3	19. 4	0. 48	1. 44
5	40	−60	36	35	95. 9	0. 3	3. 8	1. 86	1. 41
6	40	−75	48	18	98. 0	0. 5	1. 5	2. 95	1. 64
7 ^d	40	−75	48	17	98. 0	0. 5	1. 5	5. 65	1. 65

a. Conditions: complex (10 μmol), [Ph₃C][B(C₆F₅)₄] (10 μmol); [butadiene]₀: [Sc]₀ = 1000:1, solvent: toluene 5 mL; b. determined by NMR(¹³C and ¹H) and IR analyses; c. determined by GPC in THF at 40 °C against polystyrene standard; d. [butadiene]₀: [Sc]₀ = 2000:1.

3 Summary

In summary, we have demonstrated that the bis(alkyl) scandium complexes bearing the bidentate-NPN ancillary ligand can be easily synthesized, which is highly active and 1,2-selective for the polymerization of butadiene under the activation with organoborate and aluminum tris(alkyl)s generated cationic species. This represents the first example of cations act as initiators for 1,2-polymerization of butadiene, and especially, which are based on an unprecedented rare-earth metal.

参 考 文 献

[1] Wilson D J. Recent Advances in the Neodymium Catalysed Polymerisation of 1,3-Dienes[J]. *Makromol Chem Macromol*

- Symp,1993,**66**(1):273-288.
- [2] Shan C, Lin Y, Ouyang J. Single Crystal Structure of a Polymerization Active Nd-Al Bimetallic Complex[J]. *Makromol Chem*,1987,**188**(3):629-635.
- [3] Barbotin F, Spitz R, Boisson C. Heterogeneous Ziegler-Natta Catalyst Based on Neodymium for the Stereospecific Polymerization of Butadiene[J]. *Macromol Rapid Commun*,2001,**22**(17):1411-1414.
- [4] Thuilliez J, Monteil V, Spitz R, *et al.* Alternating Copolymerization of Ethylene and Butadiene with a Neodymocene Catalyst[J]. *Angew Chem Int Ed*,2005,**44**(17):2593-2596.
- [5] Evans W, Champagne T, Ziller J. Samarium *versus* Aluminium Lewis Acidity in a Mixed Alkyl Carboxylate Complex Related to Alkylaluminium Activation in Diene Polymerization Catalysis[J]. *Chem Commun*,2005:5925-5927.
- [6] Kaita S, Hou Z, Wakatsuki Y. Random- and Block-Copolymerization of 1,3-Butadiene with Styrene Based on the Stereospecific Living System: $(C_5Me_5)_2Sm(\mu-Me)_2AlMe_2/Al(i-Bu)_3/[Ph_3C][B(C_6F_5)_4]$ [J]. *Macromolecules*,2001,**34**(6):1539-1541.
- [7] Fischbach A, Klimpel M G, Widenmeyer M, *et al.* Stereospecific Polymerization of Isoprene with Molecular and MCM-48-Grafted Lanthanide(III) Tetraalkylaluminates[J]. *Angew Chem Int Ed*,2004,**43**(17):2234-2239.
- [8] Gao W, Cui D. Highly *cis*-1,4 Selective Polymerization of Dienes with Homogeneous Ziegler-Natta Catalysts Based on NCN-Pincer Rare Earth Metal Dichloride Precursors[J]. *J Am Chem Soc*,2008,**130**(14):4984-4991.
- [9] Ajellal N, Furlan L, Thomas C, *et al.* Mixed Aluminum-Magnesium-Rare Earth Allyl Catalysts for Controlled Isoprene Polymerization; Modulation of Stereocontrol[J]. *Macromol Rapid Commun*,2006,**27**(5):338-343.
- [10] Bonnet F, Visseaux M, Pereira A, *et al.* Stereospecific Polymerization of Isoprene with $Nd(BH_4)_3(THF)_3/MgBu_2$ as Catalyst[J]. *Macromol Rapid Commun*,2004,**25**(8):873-877.
- [11] Li S, Miao W, Tang T. New Rare Earth Metal Bis(alkyl)s Bearing an Iminophosphonamido Ligand. Synthesis and Catalysis toward Highly 3,4-Selective Polymerization of Isoprene[J]. *Organometallics*,2008,**27**(4):718-725.
- [12] Dudley J. Tread Rubber for High Traction Tires; US 6390163B1,2002-05-21.
- [13] Ashitaka H, Jinda H, Ueno H. Syndiotactic 1,2-Polybutadiene with Co-CS₂ Catalyst System; II. Catalysts for Stereospecific Polymerization of Butadiene to Syndiotactic 1,2-Polybutadiene[J]. *J Polym Sci Chem Ed*,1983,**21**(7):1951-1972.
- [14] Erik B Tjaden, Dale C Swenson, Richard F Jordan, *et al.* Synthesis, Structures, and Reactivity of $(R_6-acen)ZrR'_2$ and $(R_6-acen)Zr(R') + Complexes$ (R = H, F; R' = CH₂CMe₃, CH₂Ph)[J]. *Organometallics*,1995,**14**(1):371-386.

亚胺膦亚胺型稀土双烷基配合物对丁二烯 1,2-选择性聚合

刘 博^{a,b} 李世辉^b 李丹凤^b 吕 奎^b 崔冬梅^{b,c*} 孙广平^{a*}

(^a吉林大学材料科学与工程学院,教育部汽车材料重点实验室 长春 130025;

^b中国科学院长春应用化学研究所高分子物理和化学重点实验室 长春 130022;

^c常州储能材料与器件研究院 常州 213022)

摘 要 以三烷基钪 $Sc(CH_2SiMe_3)_3(THF)_2$ 和胺基膦亚胺配体为原料,经烷基消去反应合成了亚胺膦亚胺(NPN)型配体螯合钪烷基配合物。其结构用¹H NMR、¹³C NMR、元素分析和X射线衍射分析进行了表征。在助催化剂有机硼盐和烷基铝的作用下,该配合物对丁二烯聚合表现出了较高的催化活性。并且随着聚合温度的降低,催化剂的1,2-选择性也随之升高。聚合温度为-75℃时,产物的1,2-结构含量高达98.0%,聚合物的分子量为 2.95×10^4 ,分子量分布为1.65。

关键词 丁二烯,选择性,催化活性