

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/275340543>

Unprecedented 3,4-Isoprene and cis-1,4-Butadiene Copolymers with Controlled Sequence Distribution by Single Yttrium Cationic Species

CONFERENCE PAPER *in* MACROMOLECULES · DECEMBER 2014

Impact Factor: 5.8 · DOI: 10.1021/ma5019654

CITATIONS

7

READS

12

8 AUTHORS, INCLUDING:



Bo Liu

Chinese Academy of Sciences

73 PUBLICATIONS 645 CITATIONS

SEE PROFILE



Xingbao Wang

Dalian University of Technology

6 PUBLICATIONS 32 CITATIONS

SEE PROFILE

Yupeng Pan

King Abdullah City for Atomic and Renewable ...

10 PUBLICATIONS 104 CITATIONS

SEE PROFILE



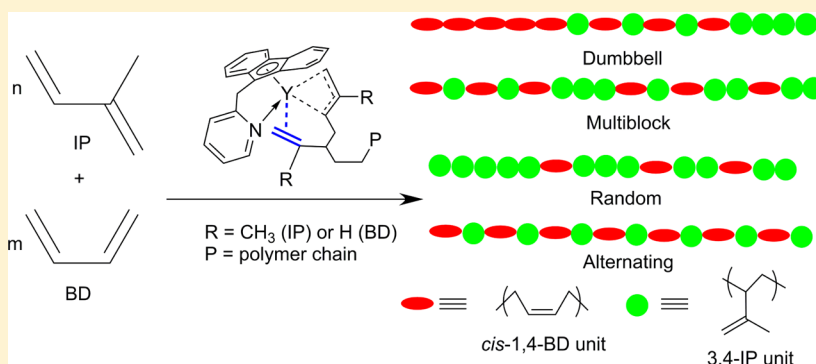
Yi Luo

118 PUBLICATIONS 1,767 CITATIONS

SEE PROFILE

Unprecedented 3,4-Isoprene and *cis*-1,4-Butadiene Copolymers with Controlled Sequence Distribution by Single Yttrium Cationic SpeciesBo Liu,^{†,⊥} Xingbao Wang,^{§,⊥} Yupeng Pan,[‡] Fei Lin,^{†,‡} Chunji Wu,[†] Jingping Qu,[§] Yi Luo,^{*,§} and Dongmei Cui^{*,†}[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China[‡]University of Chinese Academy of Sciences, Beijing 100049, China[§]State Key Laboratory of Fine Chemicals, School of Pharmaceutical, Science and Technology, Dalian University of Technology, Dalian 116024, China

S Supporting Information



ABSTRACT: Precisely controlling the stereochemistry of a copolymerization by single catalyst, and achieving copolymers with predicted sequences, is a challenging project in organometallic and macromolecular sciences. This article reports that the copolymerization of isoprene and butadiene with the 3,4- and *cis*-1,4 different regioselectivities has been accessed through employing a pyridylmethylene functionalized fluorenyl ligated yttrium cationic species. The thus unprecedented regularity combination is attributed mainly to the backbiting interaction of the penultimate unit of the polymer chain to the active central metal ion according to the DFT calculation. Moreover, the compositions can be adjusted by regulating the monomer feed ratio according to the copolymerization kinetics study.

■ INTRODUCTION

Precise control over the stereochemistry and sequence distribution of polymeric materials is a long-standing scientific topic which could provide polymers with versatile properties. Innovation of coordination catalysts has been one of the powerful strategies that has stimulated big progresses in regio- and stereoselective polymerizations to prepare special materials, such as stereoselective polymerizations of propylene and styrene, etc., to give high performance plastics¹ and regioselective polymerizations of diene monomers² to afford *cis*-1,4-polybutadiene, the most popular rubber, *cis*-1,4-polyisoprene, a promising candidate to replace natural rubber for tires manufacture,³ and the *trans*-1,4 polydienes⁴ or 3,4-polyisoprene and 1,2-polybutadiene,⁵ the important components of “green tires”. Besides these achievements in “one catalyst—one material” of homopolymerization, the stereochemistry and, in particular, the sequence distribution of the copolymerization have still been hardly controlled, although by means of the “chain-transfer” mechanism at the presence of two catalysts, some stereoregulated propylene and diene based

copolymers have been achieved.⁶ Moreover, the copolymerization that combining randomly but stereoregularly different monomer sequences into one macromolecular chain is a promising strategy to simultaneously satisfy the integral property requirements for a high performance material by exerting the synergetic effects of each monomer sequences.⁷

Herein, we report by using a single cationic pyridylmethylene functionalized fluorenyl (Flu) ligated yttrium alkyl complex (**2**) (Chart 1),⁸ the copolymerization of BD and IP gives new rubbers composed of the unprecedented *cis*-1,4-PBD and 3,4-IP regularities. The isoprene–butadiene copolymers with different regularities anticipated to possessing the excellent low-rolling resistance and good wear resistance of the *cis*-1,4 sequences and the strong wet grip property of the 1,2-/or 3,4- sequences are impossible as BD and IP bear similar structure and electronic nature, and any one catalytic system usually shows parallel

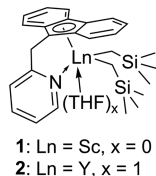
Received: September 23, 2014

Revised: November 6, 2014

Published: December 1, 2014



Chart 1. Structures of Constrained-Geometry-Configuration (CGC) Scandium (1) and Yttrium (2) Bis(alkyl) Complexes Bearing the Pyridylmethylenefunctionalized Flu Ligand



selectivity toward IP and BD polymerizations, according to the current knowledge, as far as we are aware.⁹ The DFT calculation suggested that the backbiting interaction of the penultimate double bond to the active metal center played a significant role in the process. The noncovalent interaction of the C=C double bond of penultimate unit and the metal center has always been ignored, although it was attributed to govern the high *cis*-1,4 selectivity of butadiene polymerization with the nickel catalyst¹⁰ and 3,4-selectivity of isoprene polymerization catalyzed by $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{PCy})-\text{Y}]_2(\text{CH}_2\text{SiMe}_3)\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$.¹¹ Moreover, the microstructure of the new copolymer could be adjusted swiftly from dumbbell to multiblock to random composition by varying the monomer feed ratio illustrated by the kinetics study.

RESULTS AND DISCUSSION

Upon activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Al^iBu_3 , the scandium bis(alkyl) complex **1** exhibits enriched *cis*-1,4-selectivity for IP polymerization (Table 1, entry 1). The ^{13}C NMR spectrum of the afforded polymer shows the strong signals (32.2, 26.4, and 23.4 ppm) arising from *cis*-1,4 units and the resonances at 47.9, 31.3, 29.8, and 18.6 ppm assignable to the aliphatic carbon of the isolated 3,4-IP unit within the *cis*-1,4–3,4-*cis*-1,4 sequence, but the signals between 34 and 46 ppm attributed to the *trans*-1,4 units are absent (Figure 1).¹² Theoretically, more open coordination sphere of the active metal center allows the *cis*- η^4 coordination mode of a conjugated diene monomer to afford preferably *cis*-1,4 regioselectivity as reported by the Hou and Cui groups that the cationic yttrium species stabilized by bis-(phosphinophenyl)amide^{3a} or bis(phosphino)carbazoleide^{3c} display much higher *cis*-1,4 enchainment than the corresponding smaller scandium analogue. Hence, the yttrium complex **2**

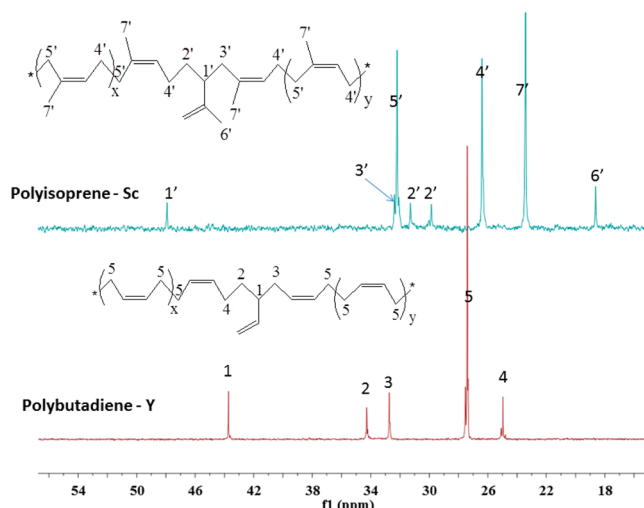


Figure 1. Aliphatic region of ^{13}C NMR spectra of polyisoprene was prepared by scandium cationic species (top) and polybutadiene was prepared by yttrium cationic species (bottom).

was synthesized and applied to IP polymerization, which, surprisingly, afforded the 3,4-unit enriched PIP rather than the expected high *cis*-1,4 sequences (Table 1, entry 2). This result intrigued us to assay the catalytic performance of complex **2** toward BD polymerization, anticipated to access 1,2-regulated PBD^{9b–d} by a rare-earth-metal precursor, a challenge of this research field.¹³ To our surprise, the resultant PBD contains around 80% *cis*-1,4 units (continuous *cis*-1,4 sequence: 27.4 ppm; *cis*-1,4 unit connecting with 1,2 unit: 32.7 and 25.0 ppm) interrupted by discrete 1,2-units (43.7 and 34.3 ppm) according to the ^{13}C NMR spectrum (Table 1, entry 3) (Figure 1).¹² To the best of our knowledge, this represents the only catalytic system that exhibits different regioselectivity for IP and BD butadiene polymerizations.

When the activators were used $[\text{PhMe}_2\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$ and AlEt_3 instead, the systems maintained the same performances (Table 1, entries 4–9). Meanwhile, the binary catalytic system composed by complex **2** and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ also shows similar selectivity to that of the ternary catalytic system (Table 1, entries 10 and 11). Hence, the monomeric cationic species $[(\eta^5\text{-Flu-CH}_2\text{Py})\text{Y}(\text{CH}_2\text{SiMe}_3)]^+$ (Flu = C_{13}H_8) was chosen as the initial active species (**A**) for

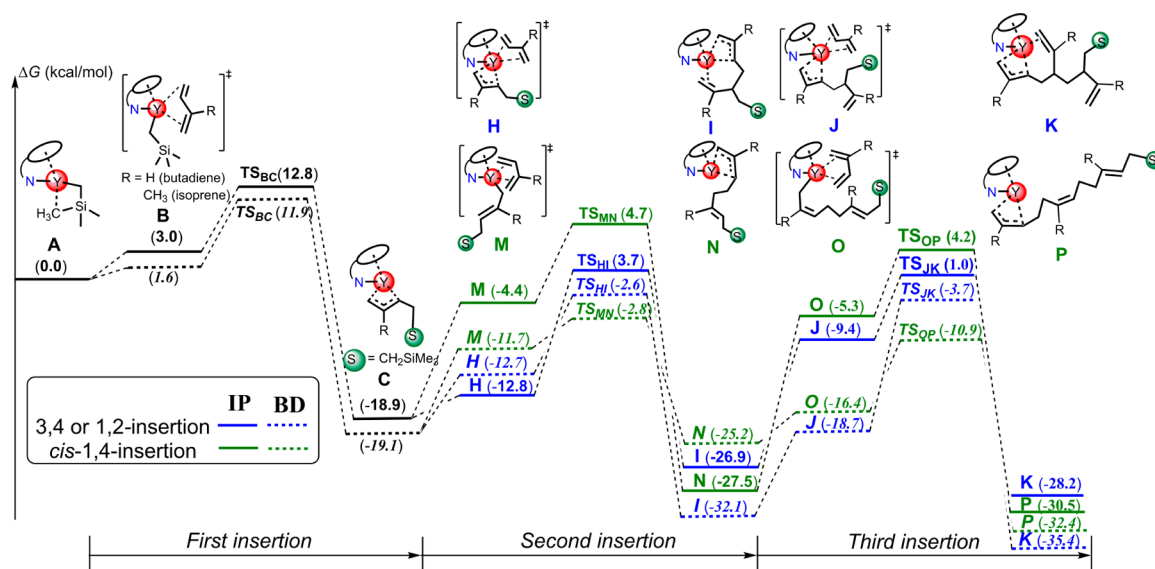
Table 1. Influence of the Metal Center and the Cocatalyst on the Selectivity toward Isoprene and Butadiene Polymerization^a

entry	cat.	Al	B	monomer	time (min)	yield ^b (%)	selectivity ^c		$M_n \times 10^{-4}$ ^d	PDI ^d
							3,4 or 1,2	<i>cis</i> -1,4		
1	1	Al^iBu_3	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	IP	6	13	17	83	40.3	2.0
2	2	Al^iBu_3	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	IP	6	51	84	16	1.46	1.6
3	2	Al^iBu_3	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	BD	1.5	78	23	77	1.56	3.8
4	2	Al^iBu_3	$[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$	IP	6	52	83	17	1.30	2.1
5	2	Al^iBu_3	$[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$	BD	1.5	80	21	79	1.78	3.9
6	2	Al^iBu_3	$\text{B}(\text{C}_6\text{F}_5)_3$	IP	90	10	86	14		
7	2	Al^iBu_3	$\text{B}(\text{C}_6\text{F}_5)_3$	BD	90	19	19	81		
8	2	AlEt_3	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	IP	90	66	65	35	1.28	1.8
9	2	AlEt_3	$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	BD	1.5	48	19	81	5.09	2.7
10	2		$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	BD	60	95	21	79	7.08	1.2
11	2		$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$	IP	90	90	90	10	7.81	1.3

^aConditions: toluene, temperature: 15 °C, cat. 10 μmol , $[\text{cat}]:[\text{Al}]:[\text{B}]:[\text{monomer}] = 1:10:1:1000$, $[\text{monomer}] = 1.5$ M. ^bIsolated yield.

^cDetermined by the ^{13}H NMR spectrum of the polymer in CDCl_3 . ^dDetermined by GPC in THF at 40 °C against a polystyrene standard.

Scheme 1. Possible Scenarios and Energy Profile of Butadiene and Isoprene Polymerization Catalyzed by Cationic $[(\eta^5\text{-Flu-CH}_2\text{Py})\text{Y}(\text{CH}_2\text{SiMe}_3)]^+$ ^a



^aBecause the activation energy of *trans*-1,4 insertion is much higher than that of *cis*-1,4 insertion and 3,4-insertion, the *trans*-1,4-insertion will not be discussed here; see Supporting Information.¹⁶

Table 2. Copolymerization of Isoprene and Butadiene at Different Feeding Ratios^a

entry	[Y] × 10 ⁴ (mol L ⁻¹)	[cat.]:[IP]:[BD] (IP/BD)	BD in polymer ^b (mol %)	selectivity ^c				M _n × 10 ⁻⁴ ^d	PDI ^d	T _g ^e
				IP		BD				
				cis-1,4	3,4	cis-1,4	1,2			
1	4.79	1:10000:400 (25)	5	12	88	>99		32.7	1.3	-2.9
2	4.29	1:10000:1200 (8.33)	12	11	89	>99		35.4	1.6	-54.1, 2.0
3	3.73	1:10000:2500 (4.0)	20	10	90	>99		39.6	1.4	-57.9, 22.4
4	2.87	1:10800:7000 (1.54)	43	8	92	86	14	54.9	1.5	-67.0, 24.8
5	1.23	1:10760:10000 (1.07)	57	7	93	81	19	61.9	1.4	-70.4, 26.0
6	2.77	1:1600:10500 (0.15)	81	5	95	77	23	40.2	1.5	-82.1

^aConditions: solvent: toluene, temperature: -20 °C, time: 2 h, [cat.]:[AlⁱBu₃]:[$\{[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\}$] = 1:10:1, isolated yield: more than 90%.

^bDetermined by the ¹H NMR spectrum of the polymer in CDCl₃. ^cDetermined by the ¹³C NMR spectrum in CDCl₃. ^dDetermined by GPC in THF at 40 °C against a polystyrene standard. ^eDetermined by DSC.

DFT calculations (Scheme 1).^{3a,5d} As shown in Scheme 1, at the initiation stage, the η^4 -*trans* coordination of BD or IP to the metal center of A (which is favored than η^4 -*cis* coordination)¹⁴ followed by insertion into Y-CH₂SiMe₃ via the transition state TS_{BC} forms the *syn* π -allyl intermediate C.¹⁵ Adoption of the second η^4 -*trans* or η^4 -*cis* coordinating monomer generates complex H or M. The 3,4- (or 1,2-) insertion of the monomer to the *syn* Y- π -allyl active species in H via TS_{HI} transition state gives intermediate I, while the 1,4-insertion of the monomer to the Y- σ -butenyl active species in M via TS_{MN} transition state affords intermediate N. I incorporates the third monomer molecule via complex J and transition state T_{JK} to afford the 3,4-regulated PIP (or 1,2-PBD) intermediate K. After coordination and insertion of the third monomer, the *cis*-1,4-regulated PIP (or PBD) intermediate P is formed via complex O and the transition state T_{OP} by following the similar reaction pathway from M → N. In the case of IP polymerization (R = CH₃), the activation energy for the 3,4-insertion (22.6 kcal/mol) is similar to *cis*-1,4 insertion (23.6 kcal/mol); however, its coordination energy is 8.4 kcal/mol lower (H: -12.8 kcal/mol vs M: -4.4 kcal/mol), suggesting the formation of 3,4-regioselectivity is preferred. Interestingly, for BD polymer-

ization (R = H), there is no obvious difference of the coordination energies (-12.7 vs -11.7 kcal/mol) or the activation energies (-16.5 vs -16.3 kcal/mol) for generating 1,2- (C → I) or *cis*-1,4 regioselectivity (C → N). Noteworthy is that there is a backbiting coordination of the C=C double bond of penultimate unit to the Y³⁺ ion in 1,2-insertion intermediate I (and K), the ligand-to-metal encapsulated thermodynamically stable product, of which the free energy is 6.9 kcal/mol lower than its *cis*-1,4 analogue N. This arouses much higher activation energy (28.4 kcal/mol) for giving the third 1,2-BD insertion intermediate K via TS_{JK} as compared to the *cis*-1,4-insertion intermediate P (14.3 kcal/mol). The cleavage of backbiting coordination of the C=C double bond of penultimate unit to the metal center being the rate-determining step of the conjugated diene polymerizations with the CpTiCl₃-MAO catalyst has been reported.¹⁷ Hence, the noncovalent interaction between the C=C double bond of the penultimate unit and the metal center in I, which is often inconspicuous, is responsible for blocking the formation of 1,2-units, thus increasing the *cis*-1,4-regulated polybutadiene with the cationic yttrium system. Such an interaction is also the

driving force for the *cis*-1,4-selectivity during the isoprene polymerization catalyzed by scandium cationic species.¹⁸

Intrigued by its unique selectivity, we employed the yttrium cationic species to copolymerize BD and IP, anticipated to achieve copolymers combining the features of *cis*-1,4-PBD and 3,4-PIP. This system was extremely active to the copolymerization and tolerant to impurities. The copolymerization could perform in toluene at $-20\text{ }^{\circ}\text{C}$ under low catalyst concentrations such as $1.23 \times 10^{-4}\text{ mol L}^{-1}$ to transfer 10 000 equiv of BD and 10 760 equiv of IP within 2 h (Table 2, entry 5). The molecular weight of the copolymer increased with the monomer feeding, and the molecular weight distribution was always narrow (Table 2, entries 1–6). The resultant copolymer had single T_g at -82.1 and $-2.9\text{ }^{\circ}\text{C}$ respectively when the IP/BD ratio was 0.15 and 25 (Table 2, entries 1 and 6), which had two T_g s between -70.4 and $26.0\text{ }^{\circ}\text{C}$ when the IP/BD ratio fell in the range of 1.07–8.33 (Table 2, entries 2–5) (SFigure 3). By increasing the IP loading, the gap between the two T_g s became narrow owing to the variety of the monomer sequence distributions along the macromolecular chains.

To date, precise prediction of the microstructure of a copolymer chain has remained a challenging project, especially in chain-growth polymerizations.¹⁹ In light of the fact that the composition and average sequence length of a comonomer within a copolymer can be calculated according to the monomers' feed ratio and reactivity ratio,²⁰ we tried to kick off the composition controlled copolymerization from kinetics study. First, the reactivity ratios of $r_{\text{BD}} = 2.29$ and $r_{\text{IP}} = 0.06$ ($T_p = 15\text{ }^{\circ}\text{C}$)²¹ were determined according to the Finemann–Ross equation (SFigure 1), and then the kinetics behaviors of the copolymerization with the monomer feed ratios (IP/BD) in the range of 0.4–25 were investigated to illustrate the exact sequence distribution of the copolymer (Table 3). When the feed ratio IP/BD was between 0.4 and 1.8, which is less than

r_{BD} , with the conversion increasing the average sequence length of BD units decreased (Table 3, entries 1–3, 4–7, and 8–9); BD achieved almost full conversion far before that of IP (Table 3, entries 3 and 7), suggesting that the resultant copolymer chain likes a dumbbell comprising the continuous BD sequence and the continuous IP sequence connected by the random BD–IP sequence. The ^{13}C NMR spectra of the copolymers isolated under low conversions show the resonances assigned to the continuous *cis*-1,4 BD (27.39 ppm), the separated 3,4-IP (47.13, 32.92, and 31.51 ppm), and 1,2-BD units (43.7, 34.3 ppm) (Figure 2, lines 1–3 from top to bottom). The smaller the IP/BD value is, the longer the BD sequence is (Table 3, entries 1, 4, and 8). At the ratios of 2.5 and 5 in the range of r_{BD} and $1/r_{\text{IP}}$, the ^{13}C NMR spectra of the obtained copolymers show the resonances at 27.55, 27.37, 25.31, and 25.18 ppm assigned to the *cis*-1,4-BD unit isolated by the 3,4-IP sequences (Figure 2, lines 4 and 5 from top to bottom), indicating that the averaging BD sequence length maintained around 1.0 in the whole polymerization process. Therefore, in the early polymerization stage when the BD content in the copolymer was around 50% (Table 3, entries 10, 11, and 13), alternating BD and IP sequence was preferred to form, which is consistent with the statistical theory that the monomer ratio (IP/BD) is in the range of r_{BD} and $1/r_{\text{IP}}$, and the alternating sequence takes precedence; with the polymerization carrying on, BD content decreased (Table 3, entries 12, 14, and 15), the continuous IP sequence should be generated that was interrupted by the discrete BD units. When the value was 25 larger than $1/r_{\text{IP}}$, on the basis of statistical probability, in the beginning, IP should prefer to homopolymerize without obvious BD insertion into the copolymer chain, which was confirmed by the experimental result that there was no resonance arising from the BD unit (Table 3, entry 16); then the single BD unit started to insert into the continuous IP sequences as the averaging BD sequence length was around 1.0 (Table 3, entry 17; Figure 2, line 6 from top to bottom), giving the copolymer with single T_g . Thus, the pseudo-alternating copolymer with the single T_g at $-49.8\text{ }^{\circ}\text{C}$ was achieved through gradually adding butadiene to the system to keep the monomers' ratio being in the range of $r_{\text{BD}}-1/r_{\text{IP}}$, which was composed solely of the *cis*-BD unit (27.55, 27.37 and 25.31, 25.18 ppm) and 3,4-IP unit (47.13, 32.92, and 31.51 ppm) (Figure 2, line 7).

The main features of green tires are low rolling resistance and abrasion loss, strong wet grip, while improvement of one property seems possible only at sacrifice of the others, which is called “devil triangle”.²² Exploring high performance rubbers where different monomer sequences should be randomly but stereoregularly incorporated into one macromolecular chain to satisfy simultaneously the integral property requirements is a long-standing scientific challenge. Here, the properties of the vulcanized mixture of this new kind of material with natural rubber were initially investigated. Normally, the values of $\tan \delta$ at 0 and $60\text{ }^{\circ}\text{C}$ of the vulcanized mixture are related to their wet skip and rolling resistance properties, respectively. The higher the value of $\tan \delta$ at $0\text{ }^{\circ}\text{C}$ is, the stronger the wet skip property is. The smaller value of $\tan \delta$ at $60\text{ }^{\circ}\text{C}$ suggested the lower rolling resistance. Comparing to the vulcanized mixture of the solution styrene–butadiene rubber (SSBR) with natural rubber, to some extent, the vulcanized mixtures of the afforded copolymer with natural rubber showed stronger wet skip and lower rolling resistance according to the measurement results (STable 3).²³

Table 3. Sequence Length of BD Unit within the Copolymer at Different Feeding Ratio and Conversion^a

entry	[IP]/[BD]	total conv ^b (%)	BD cont ^c (%)	BD conv ^d (%)	n^e
1	0.4	51	92	66	9.0
2		74	87	90	6.6
3		85	81	97	6.4
4	1.0	34	84	57	4.4
5		56	77	86	3.0
6		62	73	91	2.6
7		78	61	95	2.5
8	1.8	26	63	46	1.8
9		49	59	81	1.4
10	2.5	23	58	46	1.1
11		41	53	73	1.0
12		65	39	88	1.0
13	5.0	18	48	51	1.0
14		31	37	69	1.0
15		75	20	90	1.0
16	25	11			
17		73	3	57	1.0

^a[Y]: 0.1 mmol L⁻¹, [Y]:[Ph₃C][B(C₆F₅)₄]:[AlⁱBu₃] = 1:1:10, toluene, temperature: 15 $^{\circ}\text{C}$, [IP]:[Y] = 800–2000, [BD]:[Y] = 80–2000. ^bDetermined by the copolymer weight. ^cDetermined by the ^{13}C NMR spectrum. ^dCalculated according to the formula $\{(\text{BD content}) \times (\text{total conversion}) \times (\text{IP} + \text{BD})\}/(\text{BD})$. ^eAverage number of BD unit in the copolymer determined by the ^{13}C NMR spectrum, $n = (I_{27.3-27.6}/2 - I_{47.13} + I_{43.7-2})/I_{47.13}$.

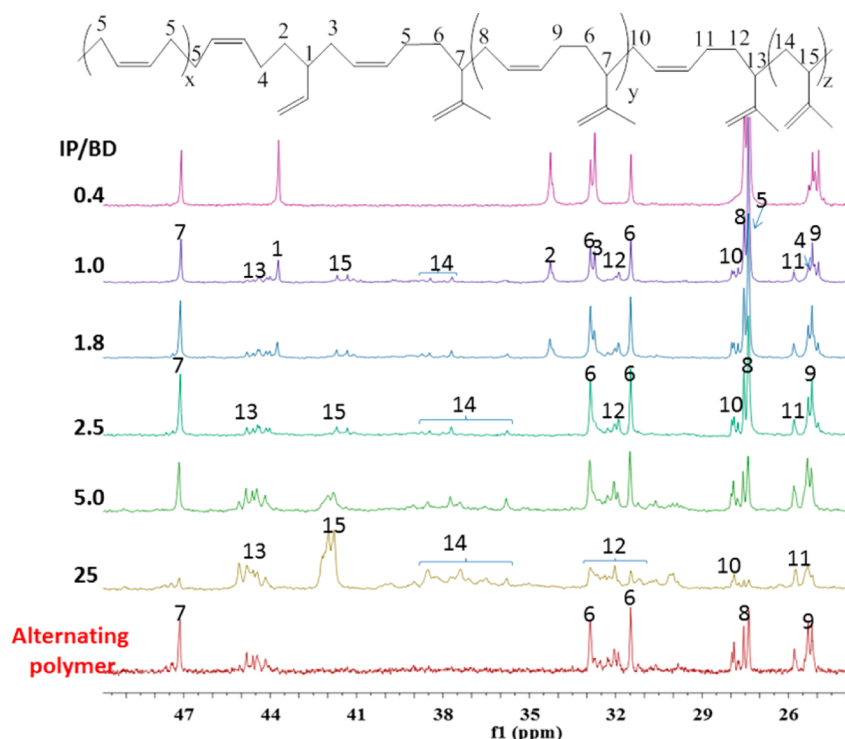


Figure 2. Aliphatic carbon region of ^{13}C NMR spectra of copolymers afforded at low yield under different IP/BD value (from top to bottom: IP/BD = 0.4, 1.0, 1.8, 2.5, 5.0, and 25) and the alternating polymer afforded through sequential monomer addition (bottom line).

CONCLUSION

New elastomeric copolymers with the unprecedented *cis*-1,4-PBD and 3,4-PIP sequences have been synthesized, for the first time, by using single yttrium cationic species, which can be attributed to the unusual mechanism involving in the noncovalent interaction between the C=C double bond of penultimate unit and the metal center according to the DFT calculation. On the basis of kinetics study, the dumbbell, multiblock and random copolymers have been obtained at different monomer feed ratios. In particular, the pseudo-alternating *cis*-1,4-BD and 3,4-IP copolymer was also accessed through gradually adding butadiene to the polymerization system. This work provides for the first time a novel strategy to realize the stereochemistry and sequence controlled copolymerization by using single catalyst system, giving a promising rubber for green tires.

EXPERIMENTAL SECTION

General Methods 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. ^1H and ^{13}C NMR spectra of polymer samples were recorded on a Bruker AV400 (FT, 400 MHz for ^1H ; 100 MHz for ^{13}C) spectrometer in CDCl_3 . The molecular weight and the molecular weight distribution of the polymers were measured by means of gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC instrument. T_g was measured through differential scanning calorimetry (DSC) analyses, which were carried out on a Mettler TOPEM TM DSC Instruments under a nitrogen atmosphere. Isoprene was dried over CaH_2 under stirring for 48 h and distilled under reduced pressure before use. Butadiene was used as received. The corresponding complexes **1** and **2** were synthesized following the literature procedures.⁸

Computational Details. All the DFT calculations were performed with the Gaussian 09 program.²⁴ The hybrid exchange-correlation functional B3PW91²⁵ was utilized. In the geometry optimizations, the

6-31G* basis set was used for H, C, and N atoms, and the Si, Sc, and Y atoms were treated by the Stuttgart/Dresden effective core potential (ECP) and the associated basis sets. As shown in previous studies,²⁶ such functional and basis sets have been fully tested and proved to be reliable for such systems. Geometries of all the species were fully optimized without symmetry constraints. The transition states were ascertained by a single imaginary frequency for the correct mode. The minima on the reaction potential energy surface were verified to have all real frequencies only. Population analysis were carried out by the natural bond orbital (NBO) formalism. Figures of three-dimensional molecular structure were prepared using CYLView.²⁷

Typical Polymerization Procedure of Isoprene. To a toluene solution of complex **2** (0.006 g, 10 μmol), the solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.010 g, 10 μmol) was added at 15 $^\circ\text{C}$. After 2 min, the Al^iBu_3 solution (0.1 mL, 1 M) was added to the above reaction solution. Then the catalytic mixture was transferred into the toluene solution (6 mL) of isoprene (0.68 g, 10 mmol). After the designated time, the reaction was terminated by addition of acidified MeOH (HCl, 10 wt %), and the polymer was precipitated in methanol and washed thoroughly. The polymer was then dried to constant weight in a vacuum oven at 40 $^\circ\text{C}$ under dynamic vacuum ($<5 \times 10^{-2}$ mbar).

Typical Polymerization Procedure of Butadiene. To a toluene solution of complex **2** (0.006 g, 10 μmol), the solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.010 g, 10 μmol) was added at 15 $^\circ\text{C}$. After 2 min, the Al^iBu_3 solution (0.1 mL, 1 M) was added to the above reaction solution. Then the catalytic mixture was transferred into the toluene solution (2.45 g, 22 wt %) of butadiene. After the designated time, the reaction was terminated by addition of acidified MeOH (HCl, 10 wt %), and the polymer was precipitated in methanol and washed thoroughly. The polymer was then dried to constant weight in a vacuum oven at 40 $^\circ\text{C}$ under dynamic vacuum ($<5 \times 10^{-2}$ mbar).

Typical Polymerization Procedure of Copolymerization of Isoprene and Butadiene. To a toluene solution of complex **2** (0.006 g, 10 μmol), the solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.010 g, μmol) was added at 15 $^\circ\text{C}$. After 2 min, the Al^iBu_3 solution (0.1 mL, 1 M) was added to the above reaction solution. Then the catalytic mixture was transferred into the toluene solution of isoprene (0.68 g, 10 mmol)

and butadiene (0.54 g, 10 mmol). After the designated time, the reaction was terminated by addition of acidified MeOH (HCl, 10 wt %), and the polymer was precipitated in methanol and washed thoroughly. The polymer was then dried to constant weight in a vacuum oven at 40 °C under dynamic vacuum ($<5 \times 10^{-2}$ mbar).

Polymerization Procedure of Copolymerization of Isoprene and Butadiene To Prepare the Alternating Copolymer. To a toluene solution of complex **2** (0.006 g, 10 μ mol), the solution of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.010 g, 10 μ mol) was added at 15 °C. After 2 min, the $\text{Al}(\text{Bu})_3$ solution (0.1 mL, 1 M) was added to the above reaction solution. Then the catalytic mixture was transferred into the mixture of isoprene (1.36 g, 20 mmol) and butadiene (0.22 g, 4 mmol). After 30 s, a toluene solution of butadiene (0.86 g, 16 mmol) was gradually added to the polymerization solution within 12 min. Then, the reaction was terminated immediately by addition of acidified MeOH (HCl, 10 wt %), and the polymer was precipitated in methanol and washed thoroughly. The polymer was then dried to constant weight (1.62 g, yield: 66%) in a vacuum oven at 40 °C under dynamic vacuum ($<5 \times 10^{-2}$ mbar).

■ ASSOCIATED CONTENT

● Supporting Information

Fineman–Ross plot, DSC curves of the copolymers, optimized cationic species A_{Sc} and A_{Y} , optimized structures of **B**, potential energy surface for Sc-isoprene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail dmcui@ciac.ac.cn; Fax (+86) 431 85262774; Tel +86 431 85262773 (D.C.).

*E-mail luoyi@dlut.edu.cn (Y.L.).

Notes

The authors declare no competing financial interest.

[†]These authors contributed equally to this work.

■ ACKNOWLEDGMENTS

This work was partially supported by the MST for “973” project No. 2015CB654702 and the NSFC for project Nos. 21374112, 51321062, 21274143, and 21361140371.

■ REFERENCES

- (1) (a) Makio, H.; Fujita, T. In *Stereoselective Polymerization with Single-Site Catalyst*; Baugh, L. S., Canich, J. A. M., Eds.; CRC Press: New York, 2008; pp 157–168. (b) Beckerle, K.; Okuda, J. In *Syndiotactic Polystyrene: Synthesis, Characterization, Processing and Applications*; Schellenberg, J., Ed.; Wiley: Schkopau, 2009; pp 125–139.
- (2) (a) Ricci, G.; Sommazzi, A.; Masi, F.; Ricci, M.; Boglia, A.; Leone, G. *Coord. Chem. Rev.* **2010**, 254, 661–676. (b) Zhang, Z. C.; Cui, D. M.; Wang, B. L.; Liu, B.; Yang, Y. *Struct. Bonding (Berlin)* **2010**, 137, 49–108.
- (3) The references reporting the *cis*-1,4-regularity is more than 99% using rare-earth metal as catalyst are summarized: (a) Zhang, L. X.; Suzuki, T.; Luo, Y.; Nishiura, M.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2007**, 46, 1909–1913; *Angew. Chem.* **2007**, 119, 1941–1945. (b) Meermann, C.; Tornroos, K. W.; Nerdal, W.; Anwender, R. *Angew. Chem., Int. Ed.* **2007**, 46, 6508–6513. (c) Fischbach, A.; Meermann, C.; Eickerling, G.; Scherer, W.; Anwender, R. *Macromolecules* **2006**, 39, 6811–6816. (d) Zimmermann, M.; Froystein, N. A.; Fischbach, A.; Sirsch, P.; Dietrich, H. M.; Tornroos, K. W.; Herdtweck, E.; Anwender, R. *Chem.—Eur. J.* **2007**, 13, 8784–8800. (e) Wang, L. F.; Cui, D. M.; Hou, Z. M.; Li, W.; Li, Y. *Organometallics* **2011**, 30, 760–767. (f) Lv, K.; Cui, D. M. *Organometallics* **2010**, 29, 2987–2993. (g) Li, D. F.; Li, S. H.; Cui, D. M.; Zhang, X. Q. *Organometallics* **2010**, 29, 2186–2193. (h) Gao, W.; Cui, D. M. *J. Am.*

Chem. Soc. **2008**, 130, 4984–4991. (i) Jian, Z. B.; Tang, S. J.; Cui, D. M. *Chem.—Eur. J.* **2010**, 16, 14007–14015.

(4) The typical references reporting the *trans*-1,4-regularity is more than 99% using rare-earth metal as are summarized: (a) Liu, H.; He, J. Y.; Liu, Z. X.; Lin, Z. G.; Du, G. X.; Zhang, S. W.; Li, X. F. *Macromolecules* **2013**, 46, 3257–3265. (b) Bonnet, F.; Visseaux, M.; Pereira, A. *Macromolecules* **2005**, 38, 3162–3169. (c) Zimmermann, M.; Tornroos, K. W.; Sitzmann, H. *Chem.—Eur. J.* **2008**, 14, 7266–7277. (d) Zimmermann, M.; Tornroos, K. W.; Anwender, R. *Angew. Chem., Int. Ed.* **2008**, 47, 775–778.

(5) The references reporting the 1,2 (or 3,4)-regularity is more than 99% using rare-earth metal as are summarized: (a) Zhang, L. X.; Luo, Y.; Hou, Z. *J. Am. Chem. Soc.* **2005**, 127, 14562–14563. (b) Du, G. X.; Wei, Y. L.; Ai, L.; Chen, Y. Y.; Xu, Q.; Liu, X. A.; Zhang, S. W.; Hou, Z. M.; Li, X. F. *Organometallics* **2011**, 30, 160–170. (c) Zhang, L. X.; Nishiura, M.; Yuki, M.; Luo, Y.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2008**, 47, 2642–2645. (d) Li, S. H.; Cui, D. M.; Li, D. F.; Hou, Z. M. *Organometallics* **2009**, 28, 4814–4822. (e) Yao, C. G.; Liu, D. T.; Li, P.; Wu, C. J.; Li, S. H.; Liu, B.; Cui, D. M. *Organometallics* **2014**, 33, 684–691.

(6) (a) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, 312, 714–719. (b) Pan, L.; Zhang, K.; Nishira, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2011**, 50, 12012–12015; *Angew. Chem.* **2011**, 123, 12218–12221. (c) Valente, A.; Stoclet, G.; Bonnet, F.; Mortreux, A.; Visseaux, M.; Zinck, P. *Angew. Chem., Int. Ed.* **2014**, 53, 4638–4641; *Angew. Chem.* **2014**, 126, 4726–4729.

(7) Nordsiek, K. H. *Kautsch. Gummi Kunstst.* **1985**, 38, 178.

(8) Pan, Y. P.; Rong, W. F.; Jian, Z. B.; Cui, D. M. *Macromolecules* **2012**, 45, 1248–1253.

(9) Some typical reference about the copolymerization of isoprene and butadiene: (a) Rong, W. F.; Liu, D. T.; Zuo, H. P.; Pan, Y. P.; Jian, Z. B.; Li, S. H.; Cui, D. M. *Organometallics* **2013**, 32, 1166–1175. (b) Bazzini, C.; Giarrusso, A.; Porri, L. *Macromol. Rapid Commun.* **2002**, 23, 922. (c) Ricci, G.; Morganti, D.; Sommazzi, A.; Santi, R.; Masi, F. *J. Mol. Catal. A: Chem.* **2003**, 204–205, 287. (d) Ricci, G.; Battistella, M.; Bertini, F.; Porri, L. *Polym. Bull.* **2002**, 48, 25.

(10) (a) Hughes, R. P.; Jack, T.; Powell, J. J. *Organomet. Chem.* **1973**, 63, 451–459. (b) Ciajolo, R.; Jama, M. A.; Tuzi, A.; Vitagliano, A. *J. Organomet. Chem.* **1985**, 295, 233–238. (c) Taube, R.; Wache, S. *J. Organomet. Chem.* **1992**, 428, 431–442. (d) Allegra, G.; Giudice, F. Lo; Natta, G.; Giannini, U.; Fagherazzi, G.; Pino, P. *Chem. Commun.* **1967**, 1263.

(11) Zhang, L. X.; Luo, Y.; Hou, Z. M. *J. Am. Chem. Soc.* **2005**, 127, 14562–14563.

(12) (a) Gronski, W.; Murayama, N.; Cantow, H.-J.; Miyamoto, T. *Polymer* **1976**, 17, 358–360. (b) Suman, P. T.; Westler, D. D. *J. Polym. Sci., Part A: Polym. Chem.* **1975**, 13, 1963–1967.

(13) Liu, B.; Li, S. H.; Li, D. F.; Lv, K.; Cui, D. M.; Sun, G. P. *Chin. J. Appl. Chem.* **2012**, 29, 1394–1398.

(14) A *cis*-coordination of monomer to active metal center is a high energy passway (see SFigure 6).

(15) Perrin, L.; Bonnet, F.; Visseaux, M.; Maron, L. *Chem. Commun.* **2010**, 46, 2965–2967.

(16) The *trans*-1,4 insertion of the second BD or IP is impossible due to its activation energy (22.9 (BD), 27.2 (IP) kcal/mol) being much higher than that of *cis*-1,4 insertion (16.3 (BD), 23.6 (IP) kcal/mol) and 1,2 (or 3,4)-insertion (16.5 (BD), 22.6 (IP) kcal/mol).

(17) Peluso, A.; Improta, R.; Zambelli, A. *Organometallics* **2000**, 19, 411–419.

(18) The free energy of **I** is lower than **N** by 1.8 kcal/mol for isoprene polymerization catalyzed by scandium cation. The coordination energy (12.7 kcal/mol) and activation energy (30.0 kcal/mol) of 3,4-insertion are much higher than those of *cis*-1,4-insertion (coordination energy: 10.9 kcal/mol; activation energy: 27.1 kcal/mol) (SFigure 9).

(19) Lutz, J.-F.; Pakula, T.; Matyjaszewski, K. *ACS Symp. Ser.* **2003**, 854, 268–282.

(20) Odian, G. In *Principles of Polymerization*, 4th ed.; Odian, G., Ed.; Wiley-Interscience: New York, 2004; pp 464–543.

(21) At $-20\text{ }^{\circ}\text{C}$, the reactivity ratios are $r_{\text{BD}} = 2.30$ and $r_{\text{IP}} = 0.05$ (SFigure 2), indicating that the temperature has little influence on the reactivity ratio.

(22) Nordsiek, K. H. *Kautsch. Gummi Kunstst.* **1985**, 38, 178.

(23) The details of the new rubber/natural rubber vulcanizates; see Supporting Information.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.

(25) (a) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, 45, 13244.

(b) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.

(26) (a) Perrin, L.; Bonnet, F.; Chenal, T.; Visseaux, M.; Maron, L. *Chem.—Eur. J.* **2010**, 16, 11376. (b) Perrin, L.; Bonnet, F.; Visseaux, M.; Maron, L. *Chem. Commun.* **2010**, 46, 2965.

(27) Legault, C. Y. *CYLview, 1.0.562beta*; Université de Sherbrooke, 2009 (<http://www.cylview.org>), accessed on March 30, 2013.