760 *Organometallics* **2011,** *30,* 760–767
DOI: 10.1021/om1009395

ORGANOMETALLICS
Article

Highly Cis-1,4-Selective Living Polymerization of 1,3-Conjugated Dienes and Copolymerization with ε-Caprolactone by Bis(phosphino)carbazolide Rare-Earth-Metal Complexes

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Received September 30, 2010

Bis(phosphino)carbazole, HL (HL = 3,6-(tBu)$_2$-1,8-(PPh$_2$)$_2$-carbazole), reacted with rare-earth-metal tris(aminobenzyl) complexes (Ln(CH$_2$C$_6$H$_4$N(Me)$_2$-o)$_3$) to afford the first PNP-carbazolide rare-earth-metal bis(alkyl) complexes, LLn(C$_6$H$_4$CH$_2$N(Me)$_2$)$_2$ (Ln=Y (**1**), Sc (**2**), Er (**3**)). The yttrium complex **1** was characterized by X-ray diffraction analysis as a solvent-free monomer, in which the carbazolide ligand coordinates to the Y^{3+} ion in a κP:κN:κP′-tridentate mode and the two aminobenzyl groups coordinate to the Y^{3+} ion in η^1C:κN-bidentate modes. Complexes **1**−**3** combined with [Ph$_3$C][B(C$_6$F$_5$)$_4$] gave cationic catalyst systems that initiated cis-1,4-polymerizations of 1,3-conjugated dienes with high activities. Especially, the system **1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] displayed excellent cis-1,4-selectivity (> 99%) and living mode at a broad range of polymerization temperatures (0−80 °C). Remarkably, the living yttrium−polydiene active species could further initiate the ring-opening polymerization of ε-caprolactone to give selectively poly(*cis*-1,4-diene)-*b*-polycaprolactone block copolymer with controllable molecular weight (M_n = (10−70) × 10^4) and narrow polydispersity (PDI = 1.15−1.47).

Introduction

Cis-1,4-regulated polydienes are one of the most important rubbers, whose rheological and mechanical properties are significantly influenced by their microstructures such as molecular weight, molecular weight distribution, and especially cis-1,4-regularity. A direct consequence of a minor increase in cis-1,4-regularity is strain-induced crystallization of raw rubbers and vulcanizates, which significantly influences mechanical properties: e.g. tensile strength, resistance to abrasion and fatigue, etc.[1] Therefore, for half a century the investigation of homogeneous catalyst systems that provide over 98% cis-1,4-selectivity and living mode has been one of the most fascinating and challenging subjects in both academic and industrial fields. The conventional Ziegler−Natta type catalysts created in the 1960s are easy to prepare, are cheap, and have been applied in industry but produce polydienes with relatively low cis-1,4-regularity (< 97%) and poorly controlled molecular weight due to multisited initiation centers.[2] Modified Ziegler−Natta catalysts based on heterometallic lanthanide methylaluminates display an obvious improvement in selectivity and control of the molecular weight distribution.[3] Lanthanidocene-mediated catalysts[4] and some modified titanium catalysts[5] exhibit excellent living mode together with high cis-1,4-selectivity, albeit at low polymerization temperatures. The cationic rare-earth-metal catalysts have been reported recently to show considerably high cis-1,4-selectivity, even at elevated temperatures.[6] However, to date catalyst systems that show both high cis-1,4-selectivity and living character are still scarce.

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 Published on Web 02/03/2011

On the other hand, incorporation of polar functional groups into nonpolar polymers endows the hydrophobic materials with remarkable adhesive, dyeing, moisture absorption, etc. surface properties, miscibility with other polymers, and rheological properties.[7] To reach this target, strategies such as modifying the nonpolar polymers with functional groups[8−10] or using nonpolar polymers as macroinitiators to incorporate polar blocks[11] have been adopted. However, the most efficient and direct method, copolymerization of nonpolar and polar monomers by using coordination catalysts, has been retarded, as the active metal centers facilitating the polymerization of nonpolar monomers are extremely oxophilic and are easily poisoned by polar monomers. The stalemate was broken by the invention of lanthanidocenes that initiate the block copolymerization of simple olefins such as ethylene with MMA (or cyclic esters).[12] A fascinating improvement[13−16] is attributed to the recent discovery of transition-metal-based systems that exhibit distinguished activity or high incorporation rate of polar monomers. In contrast, the copolymerization of conjugated dienes with polar monomers by using coordination catalysts remains less explored.[17] Although such copolymerization can be accessed by using macroinitiators via an ATRP (or anionic) mechanism,[18] the resultant copolymer usually has poor regularity and less controlled molecular weight or is a mixture of homopolymers. Therefore, copolymerization of conjugated dienes and functional monomers in a regio- and stereospecific manner has been a challenge. Obviously, the development of new catalysts that show not only specific selectivity and living character for the polymerization of dienes but also activity for the polymerization of polar monomers is required.

On the basis of our recent studies on the (co)polymerization of 1,3-conjugated dienes by using well-defined organo rare-earth-metal catalysts,[6a,b,19,20] we designed a new PNP-tridentate carbazolide ligand to stabilize rare-earth-metal dialkyl species. Although carbazole derivatives are used to support low-coordinate metals[21a,b] and transition metals,[21c−e] the multidentate carbazolide transition-metal complexes were structurally defined only recently,[21f−i] and no analogous rare-earth-metal alkyl complexes have yet been reported.[22] To date, the use of carbazolide metal complexes as polymerization catalysts has been unexplored, although the catalytic activity for Nozaki−Hiyama and other reactions has been reported.[23]

Herein we report the synthesis and characterization of unique PNP-pincer carbazolide rare-earth-metal bis(alkyl) complexes. On activation with organoborate these complexes transferred into corresponding cationic species that

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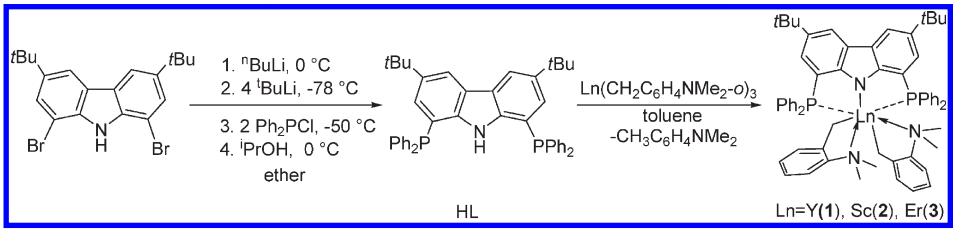
Scheme 1. Synthesis of Bis(phosphino)carbazolide Rare-Earth-Metal Bis(aminobenzyl) Complexes



showed high activity, distinguished regioselectivity, and excellent living modes for the polymerizations of dienes. More strikingly, the cationic living metal-polydiene species could further initiate the ring-opening polymerization (ROP) of the polar monomer ε-caprolactone (ε-CL) to give block copolymers of poly(*cis*-1,4-diene)-*b*-polylactone selectively.

Results and Discussion

Synthesis of PNP-Carbazolide Rare-Earth-Metal Bis(alkyl) Complexes. Rare-earth-metal alkyl complexes have attracted increasing attention in the past decade, as highly active single-component catalysts or crucial precursors of the cationic counterparts after being activated by MAO or borates, and have shown tremendous catalytic activities toward olefin polymerizations[4f,24] and specific selective polymerizations of conjugated monomers[4c,d] and polar monomers.[25] However, the preparation of such complexes usually encounters problems of salt addition, dimerization, ligand scrambling, and unpredictable C−H activation, due to the highly active character of the metal−carbon bonds and relatively less crowded steric environment of the molecules.[26] In order to overcome these drawbacks, we designed a substituted bis(phosphino)carbazole (HL, 3,6-(tBu)$_2$-1,8-(PPh$_2$)$_2$-carbazole) possessing PNP-tridentate coordination sites and "soft" and "large" phosphine atoms that were anticipated to stabilize rare-earth-metal bis(alkyl) species electronically and sterically. This PNP-tridentate carbazole was synthesized according to the modified literature procedure.[21d,27] 3,6-(tBu)$_2$-1,8-Br$_2$-carbazole was lithiated stepwise with *n*-butyllithium and then *tert*-butyllithium. A metathesis reaction of the lithiation product with PPh$_2$Cl afforded HL. Deprotonation of HL by rare-earth-metal tris(aminobenzyl) species, Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$,[28] generated the targeted bis(aminobenzyl) derivatives, LLn(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (Ln = Y (**1**), Sc (**2**), Er (**3**)) (Scheme 1). The NMR spectroscopic analyses of complexes **1** and **2** (**3** is paramagnetic) displayed the absence of the carbazole amino proton and resonances of the carbazolide moiety slightly different from those of the free ligand, suggesting that the ligand successfully chelated to the metal centers. Meanwhile, the methylene protons of the metal alkyl moieties Ln-σ-CH$_2$ gave resonances shifted downfield compared with those in the homoleptic precursors Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (Y-σ-CH$_2$: δ 1.95 vs δ 1.79; Sc-σ-CH$_2$: δ 2.39 vs δ 1.64), respectively. No resonances from THF molecules were detected, confirming the absence of solvent coordination. Meanwhile, Y−P coupling was observed in the ^{31}P NMR spectrum (J_{YP} = 27.1 Hz),[6b] suggesting that the carbazolide ligand coordinates to the Y^{3+} ion via phosphine atoms. X-ray diffraction analysis confirmed further the molecular structure of the

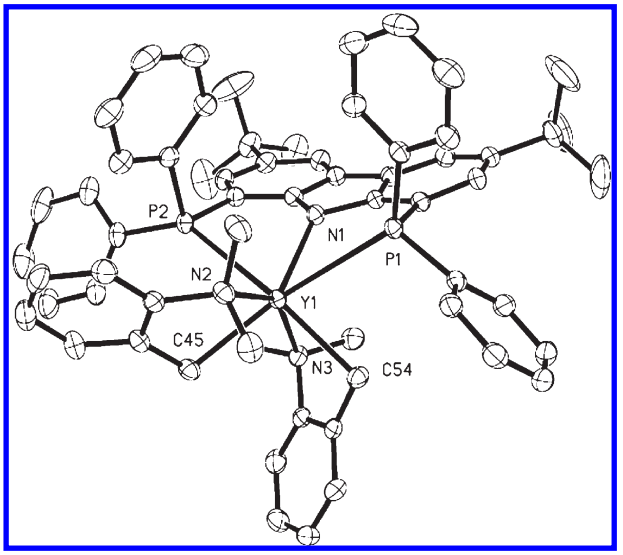


Figure 1. X-ray molecular structure of **1** with 35% probability thermal ellipsoids. Hydrogen atoms and the solvent molecule are omitted for clarity. Selected bond distances (Å) and angles (deg): Y(1)−C(45) = 2.449(4), Y(1)−C(54) = 2.444(4), N(1)−Y(1) = 2.408(3), N(2)−Y(1) = 2.588(3), N(3)−Y(1) = 2.578(3), P(1)−Y(1) = 3.1770(9), P(2)−Y(1) = 3.116(1); N(1)−Y(1)−N(3) = 84.44(10), C(54)−Y(1)−N(3) = 68.06(11), N(1)−Y(1)−N(2) = 124.83(10), C(45)−Y(1)−N(2) = 67.55(11), N(3)−Y(1)−N(2) = 149.96(10), N(1)−Y(1)−P(2) = 63.36(7), C(45)−Y(1)−P(2) = 82.54(9), N(3)−Y(1)−P(2) = 88.99(7), N(2)−Y(1)−P(2) = 98.16(7), N(1)−Y(1)−P(1) = 64.84(7), C(54)−Y(1)−P(1) = 73.83(9), N(3)−Y(1)−P(1) = 117.16(7), P(2)−Y(1)−P(1) = 118.06(3).

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Table 1. Polymerization of Isoprene and Butadiene with Complexes (1−3)/[Ph_3C][$B(C_6F_5)_4$] [a]

entry	Ln	[M]/[Ln]	temp (°C)	time (min)	conversn (%)	M_n [b] $\times 10^{-4}$	M_w/M_n	cis-1,4 [c] (%)	eff [d] (%)
1	Y	1000	25	10	100	11.7	1.07	> 99	58.1
2	Sc	1000	25	5	100	11.6	1.49	98.3	58.6
3	Er	1000	25	30	100	10.3	1.08	97.6	66.0
4	Y	1000	0	120	71	12.0	1.06	> 99	40.0
5	Y	1000	50	10	96	14.6	1.06	> 99	44.7
6	Y	1000	80	5	84	17.8	1.07	98.8	32.0
7	Y	2000	25	30	100	19.4	1.09	> 99	70.0
8	Y	3000	25	45	95	27.3	1.06	> 99	71.0
9	Y	5000	25	90	100	58.0	1.14	> 99	58.6
10	Y	10000	25	150	100	160.0	1.24	> 99	42.5
11 [e]	Y	1000	25	45	100	7.6	1.11	98.8	89.5
12 [e]	Y	1000	25	45	100	8.3	1.12	99.0	81.5
13 [e]	Y	1000	25	45	100	7.5	1.11	98.6	90.5
14 [e]	Y	1000	25	45	95	1.7	2.96	98.9	
15 [f]	Y	500	25	150	80	2.9	1.07	> 99	74.5
16 [f]	Y	1000	25	150	71	8.2	1.06	> 99	46.1

[a] Conditions: Ln, 10 μmol; B, 10 μmol (B = [Ph_3C][$B(C_6F_5)_4$]); 10/1 toluene/isoprene (v/v). [b] Determined by means of gel permeation chromatography (GPC) against polystyrene standards. [c] Measured by means of ^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$. [d] Catalyst efficiency, calculated by M_n(calcd)/M_n(measd). [e] Addition of $AlMe_3$ (entry 11), $AlEt_3$ (entry 12), Al^iBu_3 (entry 13), and $HAlEt_2$ (entry 14) at an Al to Y ratio of 10. [f] Polymerization of butadiene ([BD] = 1.67 mol/L).

yttrium complex **1** as a THF-free seven-coordinate monomer (Figure 1). The carbazolide ligand binds to the Y^{3+} ion via the two phosphine atoms and an nitrogen atom in a κP:κN:κP′-tridentate mode to form a planar pincer geometry; the Y^{3+} ion deviates slightly out of the plane owing to the steric congestion arising from the phenylphosphine groups. Meanwhile, both aminobenzyl ligands chelate to the Y^{3+} ion via nitrogen and carbon atoms in η^1C:κN-bidentate modes, with one occupying the exo position and the other occupying the endo position with respect to the carbazolide backbone plane. This is in contrast to the case for the flexible bis(phosphinophenyl)amido yttrium bis(alkyl) complex, in which the Y^{3+} ion combined with the phosphine atoms and the amino nitrogen atom to generate a tetrahedral geometry.[6b] The average Y−C (2.446 Å) and Y−P (3.146 Å) bond lengths fall in the normal ranges found in yttrium alkyl complexes[19a,20b,29] and phosphine chelated yttrium complexes, respectively.[26e,30]

(Co-)Polymerization of Isoprene and Butadiene. Complexes **1**−**3** alone were inert to the polymerization of 1,3-conjugated dienes but on activation with [Ph_3C][$B(C_6F_5)_4$] showed high activity toward isoprene (IP) polymerization. Complete conversion was achieved within 5 min for the scandium complex **2** and 10 min for the yttrium counterpart **1**. The erbium analogue **3** was slightly less active, which needed $^1/_2$ h to complete the polymerization under the same conditions. Meanwhile, all these catalyst systems exhibited high cis-1,4-selectivity (97.6−99%), among which the combination **1**/[Ph_3C][$B(C_6F_5)_4$] was the best to afford polyisoprene (PIP) with higher than 99% cis-1,4-regularity (Table 1, entries 1−3). Strikingly, this distinguished performance seemed not to be affected by the polymerization temperature. Therefore, polyisoprene with as high as 98.8% cis-1,4-regularity could be obtained when the polymerization was performed at or below 80 °C (Table 1, entries 4−6). To date, few systems can maintain their specific selectivity at high polymerization temperatures,[6a,b] indicating the thermal stability of the present active species. Hydrogenation of the obtained PIP samples with H_2 afforded perfect poly(ethylene-*alt*-propylene) rubbers.[31]

More remarkably, the catalyst system composed of yttrium complex **1** (or erbium complex **3**) and [Ph_3C][$B(C_6F_5)_4$] also exhibited a living mode. With the monomer to initiator ratios varying from 1000:1 to 10 000:1, the molecular weight of the resultant PIP increased linearly from 11.7×10^4 to 160.0×10^4, values slightly higher than the corresponding theoretical values, showing moderate to high catalytic efficiencies (42−71%). Meanwhile, the molecular weight distribution stayed in a very narrow range (PDI = 1.06−1.09), although it became broader when the monomer to initiator ratio was over 10 000 (PDI = 1.24) owing to the difficulty of monomer diffusion (Table 1, entries 7−10). It was noteworthy that addition of an excess amount of AlR_3 (Al:Y = 10:1, R = Me, Et, *i*Bu) to the binary system **1**/[Ph_3C][$B(C_6F_5)_4$] did not have an obvious influence on the catalytic performances (Table 1, entries 11−14).[32] This was in contrast to some other catalyst systems such as [$(C_5Me_5)_2$Gd][$B(C_6F_5)_4$],[4c] [2,6-(2,6-$C_6H_3R_2$N=CH)$_2$-C_6H_3]$LnCl_2(THF)_2$,[6a] [$YMe_2(thf)_5$]$^+$[BPh_4]$^-$,[6e] and (Flu-NHC)Ln(CH_2SiMe_3)$_2$ (Flu-NHC = $C_{13}H_8CH_2CH_2$(NCHCCHN)$C_6H_2Me_3$-2,4,6; Ln = Sc, Y, Ho, Lu),[33] which were inert in the absence of AlR_3, or the catalyst system [$(NCN^{dipp})Y(CH_2C_6H_4NMe_2$-*o*$)_2$]/[$Ph_3C$][$B(C_6F_5)_4$],[19a] which upon addition of $AlMe_3$ switched from iso-3,4-selectivity to cis-1,4-selectivity. This suggested that AlR_3 did not coordinate to the active metal center bearing a sterically bulky ligand. However, in contrast, addition of the aluminum alkyl hydride $HAlEt_2$ to the binary system **1**/[Ph_3C][$B(C_6F_5)_4$] led to a dramatic drop in the molecular weight of PIP due to its strong chain transfer effect.

The catalytic performance of **1**/[Ph_3C][$B(C_6F_5)_4$] for butadiene (BD) polymerization was similar to that of IP polymerization, albeit with a lower activity (Table 1, entries 15 and 16). Therefore, the random copolymer P(IP-*co*-BD)

(29) Nishiura, M.; Mashiko, T.; Hou, Z. *Chem. Commun.* **2008**, 2019–2021.

(30) (a) Miao, W.; Li, S.; Cui, D.; Huang, B. *J. Organomet. Chem.* **2007**, *692*, 3823–3834. (b) Yang, Y.; Li, S.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 671–678.

(31) The hydrogenation of polyisoprene was carried out in cyclohexane solution at 60 °C under 4 MPa H_2 atmosphere for 3 h with nickel naphthenate/aluminum triisobutyl catalyst, to give a perfect alternating copolymer of polyethylene and polypropylene (see Figures 7 and 8 in the Supporting Information).

(32) Hitzbleck, J.; Beckerle, K.; Okuda, J.; Halbach, T.; Mulhaupt, R. *Macromol. Symp.* **2006**, *236*, 23–29.

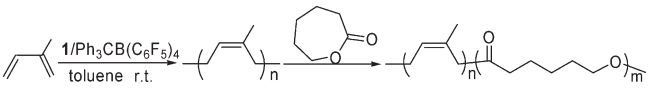
(33) Wang, B; Cui, D.; Lv, K. *Macromolecules* **2008**, *41*, 1983–1988.

Table 2. Random Copolymerization of Isoprene and Butadiene with 1/[Ph_3C][$B(C_6F_5)_4$][a]

entry	feed ratio [BD]:[IP]:[Y]	conversn (%)	M_n[b]$\times10^{-4}$	M_w/M_n	found ratio BD:IP[c]	eff[d](%)
1	1500:500:1	91	35.4	1.14	239:100	29.7
2	2000:500:1	84	44.6	1.16	304:100	26.7
3	1000:1000:1	94	31.4	1.13	80:100	36.6
4	2000:1000:1	80	58.4	1.24	153:100	24.0
5	1000:2000:1	93	59.1	1.25	45:100	29.8

[a] Conditions: **1**, 10 μmol; B, 10 μmol (B = [Ph_3C][$B(C_6F_5)_4$]); toluene, 12 mL; room temperature; 270 min. [b] Determined by means of gel permeation chromatography (GPC) against polystyrene standards. [c] Measured by means of ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$. [d] Catalyst efficiency, calculated by M_n(calcd)/M_n(measd).

Table 3. Copolymerization of Isoprene and ε-Caprolactone with 1/[Ph_3C][$B(C_6F_5)_4$] [a]



entry	feed ratio [IP]:[CL]:[Y]	T_1/T_2 (min)[b]	conversn (%)	M_n[c]$\times10^{-4}$	M_w/M_n	cis-1,4 [d]	found ratio IP:CL [d]	T_g[e] (°C)	T_m (°C)	ΔH_m (J g^{-1})
1	800:0:1	45/0	100	10.0	1.07	>99		−64.0		
2	0:1000:1	0/90	100	18.1	1.52				68.9	−61.2
3	800:300:1	45/90	100	15.4	1.15	>99	315:100	−62.4	62.9	−28.9
4	800:600:1	45/90	100	20.0	1.25	>99	150:100	−62.7	66.8	−46.8
5	1000:1000:1	60/90	99	30.7	1.28	>99	147:100	−62.3	68.0	−49.1
6	2000:1000:1	90/120	92	44.0	1.27	>99	288:100	−62.1	67.0	−32.4
7	2000:2000:1	90/120	97	61.7	1.46	>99	102:100	−62.7	67.8	−61.6
8	3000:2000:1	90/120	86	70.3	1.47	>99	122:100	−62.3	67.5	−35.5

[a] Conditions: complex **1**, 10 μmol; [B], 10 μmol (B = [Ph_3C][$B(C_6F_5)_4$]); 10/1 toluene/isoprene (v/v). [b] Polymerization time: T_1 for isoprene, T_2 for ε-CL. [c] Determined by means of gel permeation chromatography (GPC) against polystyrene standards. [d] Measured by means of ^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$. [e] Determined by differential scanning calorimetry (DSC).

could be easily synthesized by copolymerizing a mixture of IP and BD (Table 2). The composition of the copolymer could be roughly adjusted by varying the BD to IP feed ratio to be slightly higher than the BD to IP found ratio, inconsistent with the lower polymerization rate of BD. However, the molecular weight of the copolymer increased with an increase of the (IP + BD) to Y ratio. More interestingly, both the butenyl and isopentenyl sequences in the copolymer were highly cis-1,4-regulated (>99%), and the isopentenyl fragments had a head-to-tail arrangement. This means the obtained copolymer P(IP-*co*-BD) can be a kind of high-performance rubber. It is the sole characteristic of rare-earth-metal-based catalytic systems to display high cis-1,4-selectivity toward both BD and IP polymerizations simultaneously.

Block Copolymerization of Isoprene and ε-Caprolactone. Polylactone is one of the most important biodegradable and biocompatible materials in the medical industry. Incorporation of lactone into polyisoprene will increase its compatibility with other polymers when used in tires or improve its biocompatibility when used in tissue engineering to replace bacteria-susceptible natural rubber.[34] Although neutral lanthanide complexes are efficient initiators for the ring-opening polymerization of ε-CL,[35] the ionic catalytic systems show poor activity for chain propagation because of transesterification.[36] To our delight, the catalyst system **1**/[Ph_3C][$B(C_6F_5)_4$] exhibited high activity for ε-CL polymerization (Table 3, entry 2) in addition to its excellent living mode for diene polymerizations, which inspired us to attempt the copolymerization of isoprene and ε-caprolactone (ε-CL). Fortunately, when ε-CL was added to a 100% conversion IP polymerization system, PIP-*b*-PCL diblock copolymer was isolated.[37] The composition of the copolymer was close to the IP to ε-CL feed ratio. The molecular weight of the copolymer increased proportionately with the monomer to Y ratio, consistent with the theoretical value, and the molecular weight distribution remained narrow and monomodal (Figure 2). These results suggested that the yttrium−polyisoprene active species initiated the copolymerization with ε-CL with high efficiency and high-molecular-weight block copolymer could be prepared without difficulty (Table 3, entry 8, $M_n = 70.3 \times 10^4$). The DSC traces of the copolymers revealed that, with an increase in the content of

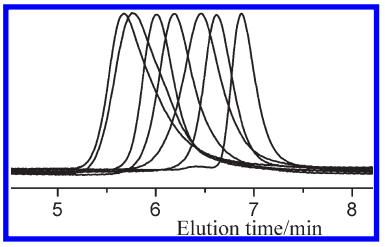


Figure 2. GPC traces of block copolymers of PIP−*b*−PCL (Table 3, entries 1 and 3−8). The rightmost is homopolyisoprene.

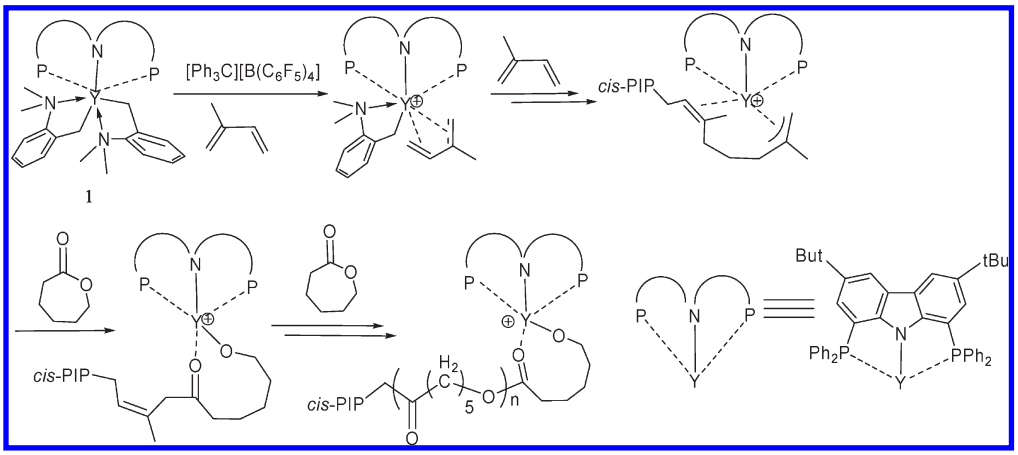
(34) Linos, A.; Berekaa, M. M.; Reichelt, R.; Keller, U.; Schmitt, J.; Flemming, H. C.; Kroppensted, R. M.; Steinbüchel, A. *Appl. Environ. Microbiol.* **2000**, 1639–1645.

(35) (a) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798–1806. (b) Nomura, N.; Taira, A.; Tomioka, T.; Okada, M. *Macromolecules* **2000**, *33*, 1497–1499. (c) Sheng, H.; Xu, F.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2007**, *46*, 7722–7724. (d) Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Dalton Trans.* **2006**, 340–350. (e) Gao, W.; Cui, D.; Liu, X.; Zhang, Y.; Mu, Y. *Organometallics* **2008**, *27*, 5889–5893.

(36) Kricheldorf, H. R.; Dunsing, R. *Makromol. Chem.* **1986**, *187*, 1611–1625.

(37) A triblock copolymer of PBD-*b*-PIP-*b*-PCL can also be obtained by sequential addition of BD, IP, and ε-CL; see Figure 21 in the Supporting Information.

Scheme 2. Probable Mechanistic Pathway for Block Copolymerization of Isoprene and ε-Caprolactone



the PIP block, the crystallinity of the PCL block became poor and its ΔH_m value was correspondingly lower, suggesting further the formation of block copolymers rather than a mixture of homopolymers.

In order to obtain information about the active species generated during the polymerization of dienes, the activation of yttrium complex **1** (LY($CH_2C_6H_4N(Me)_2$-*o*)$_2$) with [Ph_3C][$B(C_6F_5)_4$] was monitored by NMR spectroscopic techniques. According to the integral ratio in the ^{1}H NMR spectrum, the alkyl moiety $-CH_2C_6H_4N(Me)_2$-*o* in **1** was abstracted by [Ph_3C][$B(C_6F_5)_4$] to form the cationic yttrium monoalkyl species with release of the coupling product $Ph_3CCH_2C_6H_4N(Me)_2$-*o*. The resonances of the carbazolide ligand changed slightly compared with those in **1**, while the ^{31}P NMR spectrum gave a doublet for Y−P coupling at δ −3.58 (J_{Y-P} = 77.7 Hz)[6b] shifted downfield compared with δ −9.09 (J_{Y-P} = 27.1 Hz) in **1**. Moreover, the ^{19}F NMR spectrum showed the same pattern as for [Ph_3C][$B(C_6F_5)_4$], suggesting the absence of coordination between the anion $[B(C_6F_5)_4]^-$ and the cationic active species. The probable reaction pathway for the copolymerization could be simplified (Scheme 2): the IP monomer was cis-η^4 coordinated to the cationic yttrium alkyl species, inserted into the Y−CH_2 bond, and propagated to cationic yttrium polyisoprene,[2] and then ε-CL monomer coordinated to the yttrium ion via the carboxyl oxygen, which was followed by nucleophilic attack of yttrium−polyisoprene species on the carboxyl carbon to generate an yttrium−oxygen bond via cleavage of an acyl−oxygen bond (vide supra).[38] To prove this assumption, the oligomers of homopolymers of PIP and copolymers PIP-*b*-PCL were prepared.[39] According to the ^{1}H NMR spectra, the initiating aminobenzyl groups $Me_2NC_6H_4CH_2$ were detected in both oligomers, which give resonances at δ 7.21 (d), 7.17 (t), 7.11 (t), and 7.01(d) ppm for the aromatic protons, a signal at 2.73−2.70 ppm for the methylene group CH_2, and a signal at 2.68 ppm arising from NMe_2. In addition the ^{1}H NMR spectrum showed that the end group of the copolymer was CH_2OH by giving resonances around 3.68−3.65 ppm, which is consistent with the literature reported recently on the investigation of PE-*b*-PCL by Báez et al.,[40] in which hydroxyl is the end group of PE-*b*-PCL copolymers. Correspondingly, the ^{13}C NMR spectrum gives two sets of signals for PCL sequences: one set of strong signals at 173.48, 34.10, 24.56, 25.52, 28.34, and 64.11 ppm is attributed to the repeating units (−CO−$(CH_2)_5$−O−) and the other set of weak signals at 173.67, 34.20, 24.66, 25.29, 28.51, and 62.58 ppm are derived from the terminal units (−CO−$(CH_2)_5$−OH). The signal of the ketone carbonyl, $-CH_2-CH=CH(CH_3)-CH_2-C(O)(CH_2)_6-$, is detected at 210.02 ppm. This peak is the evidence for the covalent bond between PIP and PCL blocks. The above information revealed that the PIP active species initiated the polymerization of caprolactone on the carbonyl carbon via cleavage of an acyl−oxygen bond, forming a copolymer with the microstructure $(CH_3)_2NC_6H_4CH_2$−PIP−CH_2−CH=CH(CH_3)−$CH_2CO(CH_2)_5O$−PCL−$CO(CH_2)_5OH$.

As the precursor Y($CH_2C_6H_4N(Me)_2$-*o*)$_3$ combined with [Ph_3C][$B(C_6F_5)_4$] was also active in the polymerizations of dienes but was nonselective and not living, the dual catalysis of **1**/[Ph_3C][$B(C_6F_5)_4$] on the specific selective addition−polymerization of dienes and ring-opening polymerization of polar ε-CL might be attributed to the introduction of the bulky and electron-donating PNP-carbazolide ligand.

Conclusion

In summary, we have successfully prepared the first PNP-pincer carbazolide rare-earth-metal bis(alkyl) complexes without solvent coordination. These complexes, especially yttrium complex **1** on activation with [Ph_3C][$B(C_6F_5)_4$], exhibited high cis-1,4-selectivity and excellent living mode for the polymerizations of isoprene and butadiene over a broad range of polymerization temperatures. More remarkably, the cationic yttrium−polyisoprene active species could

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(39) ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) of the oligomer of homopolyisoprenes: δ 7.21 (d, J = 7.2 Hz, 1H, C_6H_4), 7.17 (t, J = 7.8 Hz, 1H, C_6H_4), 7.11 (t, J = 7.8 Hz, 1H, C_6H_4), 7.01 (d, J = 7.2 Hz, 1H, C_6H_4), 5.14 (b, 90H, CH=C, cis-1,4 PIP), 2.72−2.66 (m, 2H, $C_6H_4CH_2CH_2$), 2.65 (s, 6H, NMe_2), 2.34−2.31 (m, 2H, $C_6H_4CH_2CH_2$), 2.04 (b, 372H, CH_2, cis-1,4 PIP), 1.68 (b, 273H, CH_3, cis-1,4 PIP). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) of the oligomeric copolymers PIP-*b*-PCL: δ 7.21 (d, J = 7.8 Hz, 1H, C_6H_4), 7.16 (t, J = 7.8 Hz, 1H, C_6H_4), 7.10 (t, J = 7.8 Hz, 1H, C_6H_4), 7.01 (d, J = 7.8 Hz, 1H, C_6H_4), 5.14 (b, 166H, CH=C, cis-1,4 PIP), 4.07 (t, J = 6.6 Hz, 22H, $CO(CH_2)_4CH_2O$), 3.68−3.65 (q, J = 6.0 Hz, 2H, CH_2OH), 2.73−2.70 (m, 2H, $C_6H_4CH_2CH_2$), 2.68 (s, 6H, NMe_2), 2.32 (t, J = 7.2 Hz, 26H, $C_6H_4CH_2CH_2$, CH_2CO, and $COCH_2(CH_2)_4O$), 2.18−1.87 (overlap, 686H, mainly CH_2 of cis-1,4 PIP), 1.68−1.64 (overlap, 573H, mainly CH_3 of cis-1,4 PIP, and $COCH_2CH_2CH_2CH_2CH_2O$), 1.42−1.36 (overlap, 32H, mainly $COCH_2CH_2CH_2CH_2CH_2O$). For the ^{13}C NMR spectrum of oligomeric copolymers PIP-*b*-PCL, see Figure 22 in the Supporting Information.

(40) Báez, J. E.; Ramírez-Hernández, Á.; Marcos-Fernández, A. *Polym. Adv. Technol.* **2010**, *21*, 55–64.

initiate further the ROP of ε-CL to afford pure diblock copolymers of poly(*cis*-1,4 dienes)-*b*-PCL with designable molecular weight. This represents a well-controlled highly cis-1,4-selective copolymerization of dienes with ε-CL, which might shed new light on the design of novel catalyst precursors and further investigations of mechanisms involved in the homo- and copolymerization of dienes.

Experimental Section

General Procedure 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 with an MBRAUN SPS system. Butadiene gas was passed through a toluene solution of Al^iBu_3, followed by freezing out into cold toluene. The concentration was determined by weighing the mass difference. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 600 or 400 MHz or 300 MHz) spectrometer. NMR assignments were confirmed by $^1H-^1H$ COSY and $^1H-^{13}C$ HMQC experiments when necessary. IR spectra were recorded on a VERTEX 70 FT-IR instrument. The molecular weight and molecular weight distribution of the polymers were measured with a TOSOH HLC-8220 GPC instrument. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). DSC was performed on a METTLER TOPEM TM DSC instrument at a heating rate of 10 °C/min under an N_2 atmosphere.

X-ray Crystallographic Study. A single crystal of complex **1** suitable for X-ray analysis was manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structure was solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by full-matrix least-squares methods. The hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of 1,8-Bis(phosphino)-3,6-di-*tert*-butylcarbazole (HL). One equivalent of ^{n}BuLi (6.63 mL, 1.50 M in hexane, 10.0 mmol) was added dropwise to 1,8-dibromo-3,6-di-*tert*-butyl-9*H*-carbazole (4.37 g, 10.0 mmol) in diethyl ether (150 mL) at 0 °C. The reaction mixture was stirred for 1 h and then cooled to −78 °C, and 4 equiv of *t*BuLi (26.67 mL, 1.50 M in pentane, 40.0 mmol) was added dropwise. The reaction mixture was warmed naturally to room temperature and stirred overnight to give a pale yellow suspension. The suspension was cooled to −50 °C, and 2 equiv of chlorodiphenylphosphine (3.59 mL, 20.0 mmol) was added with continuous stirring at room temperature for 18 h. The suspension was quenched with 2-propanol (2.0 mL) at 0 °C and filtered through a pad of Celite. Removal of 2-propanol and other solvents gave a pale yellow oil, which was dissolved in a mixture of 10.0 mL of CH_2Cl_2 and 30.0 mL of pentane and cooled to −35 °C to afford HL as off-white solids (2.00 g, 30.8%). ^1H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.45 (s, 2H, 4,5-carbazole), 8.36 (s, 1H, NH), 7.76 (d, J = 8.0 Hz, 2H, 2,7-carbazole), 7.45−7.43 (m, 8H, $P(C_6H_5)_2$), 7.10−7.08 (m, 12H, $P(C_6H_5)_2$), 1.42 ppm (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): 142.56 (d, J_{CP} = 6.0 Hz, *ipso*-carbazole), 140.55 (d, J_{CP} = 9.1 Hz, *ipso*-carbazole), 135.74 (d, J_{CP} = 10.1 Hz, *ipso*-carbazole), 133.10 (d, J_{CP} = 19.1 Hz, $P(C_6H_5)_2$), 130.25 (d, J_{CP} = 19.1 Hz, *ipso*-$P(C_6H_5)_2$), 128.66−128.54 (m, $P(C_6H_5)_2$), 122.65 (s, 2,7-carbazole), 117.62 (s, 4,5-carbazole), 116.45 (d, J_{CP} = 11.1 Hz, *ipso*-carbazole), 34.74 (s, $C(CH_3)_3$), 31.84 ppm (s, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): δ −14.87 ppm (s, 2P). Anal. Calcd for $C_{44}H_{43}NP_2$: C, 81.58; H, 6.69; N, 2.16. Found: C, 81.09; H, 6.44; N, 1.89.

Synthesis of $LY(CH_2C_6H_4NMe_2\text{-}o)_2$ (1). Under a nitrogen atmosphere, HL (0.26 g, 0.40 mmol), $Y(CH_2C_6H_4NMe_2\text{-}o)_3$ (0.20 g, 0.40 mmol), and 30.0 mL of toluene were mixed in a Schlenk tube with a Teflon stopcock and heated to 50 °C for 4 h and 70 °C for 3 h. Filtration and concentration afforded a viscous solution. The solution was kept at room temperature for several hours to give yellow prismatic crystals of **1** (0.20 g, 50.1%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.56 (s, 2H, 4,5-carbazole) 7.78 (dd, J = 7.6 Hz, 1.6 Hz, 2H, 2,7-carbazole), 7.66−7.63 (m, 8H, $P(C_6H_5)_2$), 7.14 (br, 12H, $P(C_6H_5)_2$), 7.00 (t, J = 6.8 Hz, 2H, γ-$CH_2C_6H_4$), 6.94 (d, J = 7.2 Hz, 2H, α-$CH_2C_6H_4$), 6.79 (t, J = 7.6 Hz, 2H, β-$CH_2C_6H_4$), 6.72 (d, J = 8.0 Hz, 2H, δ-$CH_2C_6H_4$), 2.18 (s, 12H, NMe_2), 1.95 (s, 4H, CH_2), 1.49 ppm (s, 18H, CMe_3). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 155.97 (d, J_{CP} = 25.1 Hz, *ipso*-carbazole), 145.98 (s, *ipso*-carbazole), 143.85 (s, *ipso*-C_6H_4), 141.44 (s, *ipso*-C_6H_4), 135.44 (d, J_{CP} = 10.1 Hz, *ipso*-carbazole), 134.42 (d, J_{CP} = 14.1 Hz, $P(C_6H_5)_2$), 129.65 (s, α-*C*-C_6H_4), 129.06−128.26 (m, $P(C_6H_5)_2$), 127.28 (s, γ-$CH_2C_6H_4$), 126.49 (s, 2,7-carbazole), 119.57 (s, 4,5-carbazole), 119.50 (s, β-$CH_2C_6H_4$), 118.70 (s, δ-$CH_2C_6H_4$), 117.16 (d, J_{CP} = 12.1 Hz, *ipso*-carbazole), 53.98 (d, J_{YC} = 28.1 Hz, CH_2), 45.87 (s, NMe_2), 35.53 (s, CMe_3), 32.77 ppm (s, CMe_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 25 °C): δ −9.09 ppm (d, J_{YP} = 27.1 Hz, 2P). Anal. Calcd for $C_{62}H_{66}N_3P_2Y$: C, 74.17; H, 6.63; N, 4.19. Found: C, 73.70; H, 6.25; N, 3.67.

Synthesis of $LSc(CH_2C_6H_4NMe_2\text{-}o)_2$ (2). By a procedure similar to that described for the preparation of **1**, treatment of $Sc(CH_2C_6H_4NMe_2\text{-}o)_3$ (0.19 g, 0.40 mmol) with HL (0.26 g, 0.40 mmol) gave yellow crystals of **2** (0.15 g, 41.0%). ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.57 (s, 2H, 4,5-carbazole), 7.66 (d, J = 6.8 Hz, 2H, 2,7-carbazole), 7.43−7.44 (m, 8H, $P(C_6H_5)_2$), 7.11 (br, 12H, $P(C_6H_5)_2$), 6.96 (d, J = 6.9 Hz, 4H, α,γ-$CH_2C_6H_4$), 6.83−6.89 (m, 2H, β-$CH_2C_6H_4$), 6.77 (d, J = 8.4 Hz, 2H, δ- $CH_2C_6H_4$), 2.39 (s, 4H, CH_2), 2.41 (s, 12H, NMe_2), 1.47 ppm (s, 18H, CMe_3). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ 156.07 (d, J_{CP} = 25.6 Hz, *ipso*-carbazole), 148.15 (s, *ipso*-C_6H_4), 147.53 (s, *ipso*-carbazole), 142.06 (s, *ipso*-C_6H_4), 136.43 (d, J_{CP} = 3.0 Hz, *ipso*-carbazole), 134.43 (d, J_{CP} = 14.3 Hz, $P(C_6H_5)_2$), 131.90 (s, C_6H_4), 129.57−128.18 (m, $P(C_6H_5)_2$), 126.96 (s, 2,7-carbazole), 126.14 (s, C_6H_4), 121.45 (s, C_6H_4), 119.10 (s, C_6H_4), 118.50 (s, 4,5-carbazole), 117.80 (d, J_{CP} = 6.8 Hz, *ipso*-carbazole), 59.10 (br, CH_2), 46.59 (s, NMe_2), 35.47 (s, CMe_3), 32.67 ppm (s, CMe_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 25 °C): δ −12.61 ppm. Anal. Calcd for $C_{62}H_{66}N_3P_2Sc$: C, 77.56; H, 6.93; N, 4.38. Found: C, 77.01; H, 6.57; N, 4.11.

Synthesis of $LEr(CH_2C_6H_4NMe_2\text{-}o)_2$ (3). By a procedure similar to that described for the preparation of **1**, treatment of $Er(CH_2C_6H_4NMe_2\text{-}o)_3$ (0.24 g, 0.40 mmol) with HL (0.26 g, 0.40 mmol) afforded yellow solids of **3** (0.18 g, 43.6%). Anal. Calcd for $C_{62}H_{66}N_3P_2Er$: C, 68.80; H, 6.15; N, 3.88. Found: C, 68.41; H, 5.86; N, 3.46.

Monitoring the Reaction of Complex 1 or 2 with $[Ph_3C][B(C_6F_5)_4]$ by NMR Spectroscopic Techniques. In a glovebox, complex **1** (20.0 mg, 0.02 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (18.6 mg, 0.02 mmol) were dissolved in C_6D_6, respectively. The combined solutions were transferred into an NMR tube. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 8.74 (s, 2H, 4,5-carbazole), 7.87−7.86 (m, 2H, 2,7-carbazole), 7.47 (d, J = 7.2 Hz, 6H, Ph_3C), 7.45 (b, 8H, Ph_2P), 7.24−7.08 (m, 21H, Ph_3C, Ph_2P), 7.07 (m, 2H, $CH_2C_6H_4$-NMe_2), 6.98 (d, J = 8.0 Hz, 2H, $CH_2C_6H_4NMe_2$), 6.88 (d, J = 8.0 Hz, 2H, $CH_2C_6H_4NMe_2$), 6.77 (t, J = 8.0 Hz, 2H, CH_2-$C_6H_4NMe_2$), 2.56 (s, 6H, NMe_2), 2.40 (s, 2H CH_2), 2.39 (s, 2H, CH_2), 2.36 (s, 6H, NMe_2), 1.48 (s, 18H, Me_3C). ^{13}C NMR

(100 MHz, C_6D_6, 25 °C): δ 154.97 (s, *ipso*-carbazole), 149.62 (d, J = 248.41 Hz, 8C, $B(C_6F_5)_4$), 148.46 (s, *ipso*-$(C_6H_5)_3C$), 145.05 (s, *ipso*-C_6H_4), 143.38 (d, J = 20.1 Hz, *ipso*-carbazole), 139.36 (d, J = 244.36 Hz, $B(C_6F_5)_4$), 137.61 (d, J = 239.33 Hz, $B(C_6F_5)_4$), 133.81 (d, J = 14.1 Hz, *ipso*-carbazole), 133.14 (s, *ipso*-C_6H_4), 131.78 (d, J=28.2 Hz, *ipso*-$P(C_6H_5)_2$), 131.24 (s, 2,7-carbazole), 130.82 (s, $(C_6H_5)_3C$, $P(C_6H_5)_2$), 130.36 (s, C_6H_4), 130.11−128.26 (m, $P(C_6H_5)_2$, $(C_6H_5)_3C$, *ipso*-C_6H_4), 127.61, 127.29 (s, C_6H_4), 126.52 (s, *ipso*-$B(C_6F_5)_4$), 123.90, 123.51 (s, C_6H_4), 122.01 (d, J = 15.1 Hz, *ipso*-carbazole), 121.40 (s, 4,5-carbazole), 121.39, 120.78 (s, C_6H_4), 59.33 (s, CH_2), 57.74(s, $(C_6H_5)_3C$), 51.30 (s, CH_2), 45.56 (s, NMe_2), 44.59 (s, NMe_2), 35.55 (s, CMe_3), 32.44 (s, CMe_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 25 °C): δ −3.58 (d, J_{YP} = 77.7 Hz, 2P). ^{19}F NMR (376.3 MHz, C_6D_6, 25 °C): δ −55.29 (br, 8F, *o*-$B(C_6F_5)_4$), −85.68 (t, J = 20.7 Hz, 4F, *p*-$B(C_6F_5)_4$), −89.64 ppm (br, 8F, *m*-$B(C_6F_5)_4$). ^1H NMR for **2**/$[Ph_3C][B(C_6F_5)_4]$ (400 MHz, C_6D_6, 25 °C): δ 8.60, 8.55 (ss, 2H, 4,5-carbazole), 7.68−7.66 (m, 2H, 2,7-carbazole), 7.47 (d, J = 8.0 Hz, 6H, Ph_3C), 7.44 (b, 8H, Ph_2P), 7.24−7.03 (m, 23H, Ph_3C, Ph_2P, $CH_2C_6H_4NMe_2$), 6.99 (t, J = 8.0 Hz, 1H, $CH_2C_6H_4NMe_2$), 6.91 (t, J = 8.0 Hz, 1H, $CH_2C_6H_4NMe_2$), 6.82 (b, 1H, $CH_2C_6H_4NMe_2$), 6.78 (d, J = 8.0 Hz, 1H, $CH_2C_6H_4NMe_2$), 6.74 (b, 1H, $CH_2C_6H_4NMe_2$), 6.70 (t, J = 8.0 Hz, 2H, $CH_2C_6H_4NMe_2$), 2.41 (s, 6H, NMe_2), 2.39 (s, 2H, CH_2), 2.36 (s, 6H, NMe_2), 2.29 (s, 2H CH_2), 1.42, 1.43 (ss, 18H, Me_3C). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 25 °C): δ −3.58 (s, 1P), −5.76 ppm (s, 1P). ^{19}F NMR (282.3 MHz, C_6D_6, 25 °C): δ −55.41 (br, 8F, *o*-$B(C_6F_5)_4$), −85.46 (t, J = 21.2 Hz, 4F, *p*-$B(C_6F_5)_4$), −90.48 ppm (br, 8F, *m*-$B(C_6F_5)_4$).

Polymerization of Isoprene with 1/[Ph_3C][$B(C_6F_5)_4$]. Under a nitrogen atmosphere, complex **1** (10.0 μmol in 8.0 mL toluene) and $[Ph_3C][B(C_6F_5)_4]$ (10.0 μmol in 2.0 mL of toluene) were placed into a 25.0 mL flask. Then 1.00 mL (0.68 g, 10.0 mmol) of isoprene was added and vigorously stirred for 10.0 min. The viscous solution was poured into a large quantity (60.0 mL) of ethanol to give polyisoprene solids that were dried under vacuum to a constant weight (0.68 g, 100%). The polymerization of butadiene was carried out by a similar procedure.

Copolymerization of Isoprene and ε-Caprolactone with 1/[Ph_3C][$B(C_6F_5)_4$]. Under a nitrogen atmosphere, **1** (10.0 μmol in 8.0 mL toluene) and $[Ph_3C][B(C_6F_5)_4]$ (10.0 μmol in 2.0 mL of toluene) were placed in a 25.0 mL flask. Isoprene (0.54 g) was added into the flask, and the polymerization was carried out for 45.0 min with rapid stirring. Then ε-caprolactone (0.36 g) was added to the above system and polymerization was continued for another 90.0 min. The viscous reaction mixture was poured into a large quantity (100 mL) of ethanol to give white solids of a copolymer that were dried to a constant weight (0.90 g, 100%).

Acknowledgment. We thank the National Natural Science Foundation of China (Project Nos. 20934006 and 20910102005). The Ministry of Science and Technology of China for (Project Nos. 2005CB623802 and 2009AA03Z501), and a Grant-in-Aid for Scientific Research (S) (No. 21225004) from the Japan Society for the Promotion of Science (JSPS) for financial support.

Supporting Information Available: Figures, tables, and a CIF file giving the ^1H NMR spectrum of complex **1**, the ^1H and ^{13}C NMR spectra and DSC and GPC traces of selected PIP, PBD, PIP-*b*-PCL, and PBD-*b*-PIP-*b*-PCL samples, and X-ray diffraction analysis data and refinement details for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.