ORGANOMETALLICS

Highly 3,4-Selective Living Polymerization of Isoprene and Copolymerization with ε -Caprolactone by an Amidino N-Heterocyclic Carbene Ligated Lutetium Bis(alkyl) Complex

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Supporting Information



ABSTRACT: The amidino-modified N-heterocyclic carbene ligated lutetium bis(alkyl) complex 1, (Am-NHC)Lu(CH₂SiMe₃)₂, was synthesized by treatment of (AmH-NHC-H)Br ((2,6-ⁱPrC₆H₃N=C(C₆H₅)NHCH₂CH₂(NCHCHN(C₆H₂Me₃-2,4,6)CH)-Br) with ((trimethylsilyl)methyl)lithium (LiCH₂SiMe₃) and lutetium tris(alkyls) (Lu(CH₂SiMe₃)₃(THF)₂) via doubledeprotonation reactions and characterized by NMR spectroscopy and X-ray diffraction analysis. Under activation of an organoborate, complex 1 exhibited distinguished catalytic performance for the polymerization of isoprene with respect to high activity, 3,4-regioselectivity (99.3%), and livingness mode. In contrast to the systems reported to date, this system seemed not to be affected obviously by the polymerization temperature (0–80 °C), solvents, monomer-to-initiator ratios (500–5000), and type of organoborate. The resultant polymers have high glass-transition temperatures (38–48 °C) and moderate syndiotacticity (racemic enchainment triad *rr* 45%, pentad *rrrr* 20%). In addition, the living lutetium–polyisoprene active species could further initiate the ring-opening polymerization of ε -caprolactone to give selectively the poly(3,4-isoprene)-*b*-polycaprolactone block copolymers with controllable molecular weight (from 4.9 × 10⁴ to 10.2 × 10⁴) and narrow polydispersity.

INTRODUCTION

It is well-known that 3,4-regulated polyisoprene (PIP) is a very important component of high-performance rubbers because of its excellent wet-skid resistance and low rolling resistance.¹ Unlike its *cis*-1,4- and *trans*-1,4-regulated PIP analogues that can be found in natural rubbers, 3,4-regulated PIP can only be obtained by artificial synthesis. For the past half a century, isoprene (IP) polymerizations have attracted extensive research interest and made considerable progress. For instance, the Ziegler–Natta catalyst systems,^{2,3} f- and d-block element metallocenes,⁴⁻⁶ constrained-geometry-conformation rare-earth-metal allyl complexes,⁷ non-Cp (Cp = cyclopentadienyl and its derivatives) ligated lanthanide alkyl aluminates,⁸ β -diketiminates,⁹ and pincer type¹⁰ rare-earth-metal complexes have been thoroughly investigated to provide *cis*-1,4-selectivity. In the meantime, catalyst systems of Ln(allyl)₂Cl(MgCl₂)₂/AlR₃,¹¹ Cp*Nd(BH₄)₂(THF)₂/Mg(ⁿBu)₂)¹² TiCl₄–AlR₃ and

VCl₃–AlR₃,¹³ (C₅Me₅)Ln(AlMe₄)₂ (Ln = Y, La, Nd),¹⁴ quinolyl anilido rare-earth-metal bis(alkyl) precursors and [N(PPh₂NPh)₂] Ln(CH₂SiMe₃)₂ (Ln = Sc, Y, Lu),¹⁵ and [(*S*,*S*)-BOPA]Ln(CH₂SiMe₃)₂ ((*S*,*S*)-BOPA = (*S*,*S*)-bis-(oxazolinylphenyl)amido; Ln = Sc, Lu)¹⁶ have been invented to give *trans*-1,4-selectivity. Except for these achievements, the number of 3,4-selective catalyst systems has remained very small, as IP usually prefers to coordinate to a metal center in a η^4 -*cis*-1,4-mode (two site) under generation of 1,4-configuration; thus, a 3,4-selectivity means IP coordination to a sterically bulky active metal center in a η^2 single site.¹⁷ Up to now, efficient 3,4-selective systems have been the patented organolithium and ferric acetylacetate and transition-metal complexes such as AlEt₃-Ti(OR)₄, (dmpe)₂CrCl₂-MAO¹⁸

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Scheme 1. Synthesis of Amidino N-Heterocyclic Carbene Lutetium Bis(alkyl) Complex 1



(dmpe = 1,2-bis(dimethylphosphino)ethane), and ferric complexes chelated by nitrogen ligands,¹⁹ among which few cases exhibit 3,4-selectivity of over 90%. Only very recently has significant progress been made in the 3,4-selective polymerization of isoprene by using rare-earth-metal complexes bearing half-sandwich ligands such as [{Me₂Si(C₅Me₄)(PCy)}-YCH₂SiMe₃]₂²⁰ (Cy = cyclohexyl) and fluorenyl N-heterocyclic carbene ligated rare-earth-metal precursors,²¹ and the rare-earth-metal complexes attached to non-Cp ligands such as the NCN-yttrium complex [(PhC(NC₆H₄⁻¹Pr₂-2,6)₂)Y(o-CH₂C₆H₄-NMe₂)₂],²² NPN ligand stabilized rare-earth-metal bis(alkyls),²³ scandium aminopyridinates,²⁴ and cationic rare-earth-metal alkyl complexes bearing iminoamido ligands,²⁵ some of which showed unprecedented high regio- and stereoselectivities;^{20,22} however, few of these systems show both high 3,4-selectivity and living characteristics.^{21,25}

On the other hand, a great variety of block copolymers have been used as phase compatibilizers for blending incompatible polymers.²⁶ To obtain such block copolymers, the most efficient method is via the copolymerization of polar and nonpolar monomers; however, this 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 has been broken by the invention of lanthanidocenes that initiate the block copolymerization of simple olefins such as ethylene with MMA (or cyclic esters).²⁷ Recently, transition-metal-based systems have been demonstrated to possess high activities and high incorporation rates of polar monomers.²⁸ Nevertheless, the copolymerization of conjugated dienes with polar monomers by using coordination catalysts has been less explored.²⁹ Diblock copolymers comprising a poly(diene) block and a poly(polar monomer) block such as $poly(\varepsilon$ -caprolactone) (PCL) have been known for a long time and are usually synthesized by a standard method involving anionic living diene polymerization by using alkyllithium in the first stage and sequentially adding ε -CL in the second stage. However, this method has some disadvantages, such as chain termination by alkyl cleavage and

transesterification that occurs during the second polymerization stage when ε -CL is present. In addition, the thus obtained polydiene building blocks have low regiotacticity.³⁰ Therefore, the design of new catalysts for polymerizing dienes in a specifically selective living coordination polymerization process and further initiating the polymerization of polar monomers is still urgently required and challenging.

Herein, we report that a lutetium bis(alkyl) complex attached to an amidino-modified N-heterocyclic carbene ligand, upon activation with organoborate, initiates the living polymerization of isoprene with high activity, high 3,4-selectivity, and medium syndioselectivity. The resultant cationic living metal—polydiene species could further initiate the ring-opening polymerization (ROP) of the polar monomer ε -CL to selectively provide the first block copolymer of poly(3,4-IP)-*b*-poly(ε -CL).

RESULTS AND DISCUSSION

Synthesis and Characterization of Complex 1. The NHC-amine hydrobromide compound $(NH_2CH_2CH_2(NCHCHN(C_6H_2Me_3-2,4,6)CH)Br)$ ·HBr was synthesized from 1-mesitylimidazole and 2-bromoethylamine hydrobromide according to a literature procedure.³¹ Sequential treatment of the NHC-amine hydrobromide with NEt₃ and $C_6H_5C(Cl)N(C_6H_3Pr_2-2,6)$ gave the amidino-modified imidazolium bromide (AmH-NHC-H)Br in high yield (79%) (Scheme 1). The ¹H NMR spectrum of (AmH-NHC-H)Br exhibited a singlet at δ 10.38 ppm, typical for the ylidene proton NHC-H. The two discrete triplet resonances at δ 5.13 and 4.28 ppm could be attributed to the ethylene protons. (AmH-NHC-H)Br was treated with LiCH₂SiMe₃ to afford the ethylene-bridged amidino N-heterocyclic carbene AmH-NHC. AmH-NHC reacted with the lutetium tris(alkyl) (Lu- $(CH_2SiMe_3)_3(THF)_2$ to give the rare-earth-metal bis(alkyl) complex (Am-NHC)Lu(CH₂SiMe₃)₂ (1) via alkane elimination. The ¹H NMR spectrum of complex 1 reveals that the characteristic resonance of the ylidene proton from the ligand disappears. The methylene protons of LuCH₂SiMe₃ species are diastereotopic, appearing as complicated resonances with two discrete AB spins in the upfield regions: $\delta -0.62/-0.65$ and -0.82/-0.85. The ylidene carbon gives a characteristic singlet at δ 199.66 ppm, comparable to δ 199.18 ppm found in the NHC-containing complex (Flu-NHC)Lu(CH₂SiMe₃)₂,²¹ suggesting the formation of a linkage between the lutetium ion and the carbene carbon Lu–C. The molecular structure of complex **1** in the solution state illustrated by X-ray diffraction analysis was consistent with that in the solid state, as shown in Figure 1.



Figure 1. Molecular structure of 1 (hydrogen atoms and solvent molecule are omitted for clarity). Selected bond lengths (Å) and angles (deg) for complex 1: Lu(1)-N(1) 2.352(3), Lu(1)-N(2) 2.260(4), Lu(1)-C(22) 2.516(4), Lu(1)-C(34) 2.337(5), Lu(1)-C(38) 2.359(5); N(1)-Lu(1)-N(2) 57.55(12), N(1)-Lu(1)-C(22) 131.42(13), N(1)-Lu(1)-C(34) 100.62(14), N(1)-Lu(1)-C(38) 108.14(15), N(2)-Lu(1)-C(38) 122.15(16), C(22)-Lu(1)-C(34) 123.89(16), N(2)-Lu(1)-C(38) 101.84(16), C(34)-Lu(1)-C(38) 113.59(16), C(19)-N(1)-Lu(1) 92.3(2), C(19)-N(2)-Lu(1) 96.7(3).

The Lu³⁺ ion is bounded by the NNC-tridentate chelating ligand and two alkyl CH₂SiMe₃ moieties, generating a twisted-tetragonal geometry. Complex 1 is free of THF, in contrast to the THF-solvated benzamidinate complex [PhC(NAr)₂]Y-(CH₂SiMe₃)₂(THF) (Ar = $C_6H_3^{i}Pr_2-2,6$),³² owing to the strong electron-donating effect of the ylidene carbon. The Lu(1)- $C_{carbene}$ bond length is 2.516(4) Å, comparable to the corresponding Lu- $C_{carbene}$ bond lengths of 2.443(3) and 2.431(3) Å in the complexes (Ind-NHC)Lu(CH₂SiMe₃)₂³³ and (Flu-NHC)Lu(CH₂SiMe₃)₂²¹ respectively. The bond lengths of Lu(1)-N(1) (2.352(3) Å) and Lu(1)-N(2) (2.516(4) Å) fall in the normal range reported previously.³²

Polymerization of Isoprene. Complex 1 alone was inert to the polymerization of IP and upon activation with $[(Ph_3C)][(B(C_6F_5)_4)]$ showed a high activity to transfer 500 equiv of IP within 30 min at room temperature, which is among the highest activities reported to date.^{22,25} The reaction temperature had some influence on the activity of IP polymerization. When the polymerization was performed at a lower temperature $(0 \ ^{\circ}C)$ while other conditions were kept similar, the activity of polymerization decreased such that monomer conversion was only 94% within 120 min. In contrast, the catalytic activity increased at elevated temperatures such that a complete conversion occurred in 20 min at 40 °C, 15 min at 60 °C, and 10 min at 80 °C (Table 1, entries 7–10). In addition, this catalytic system was highly efficient, such that by increasing stepwise the monomer to catalyst ratio from 500:1 to 5000:1, the polymerization performed readily, albeit with prolonged polymerization times, and the molecular weight of the obtained PIP increased correspondingly from 3.69×10^4 to 49.2×10^4 (Table 1, entries 1–6).

Furthermore, the system exhibited distinguished 3,4selectivity (98.7%) at room temperature, which improved slightly to 99.3% at a lower polymerization temperature of 0 °C and seemed not to be affected obviously at elevated temperatures up to 80 °C (96.7%) (Table 1, entries 7–10). Although the types of solvents affected the catalyst activity significantly, such that a complete conversion of IP took 30 min by using chlorobenzene as the polymerization media but 120 min in toluene and 240 min for a 90% conversion in 1-hexane, which had almost no effect on the 3,4-selectivity. It was

Table 1. I orymetization of isoprene using Datenum Complex 1 under Various Conditions	Table	1. Pol	ymerization	of 1	lsoprene	using	Lutetium	Complex	x 1	under	Various	Conditions
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entry	[IP]/[Lu]	temp (°C)	time (min)	yield (%)	3,4 ⁶	$M_{\rm n,calcd}^{\ \ c} \times 10^{-4}$	$M_{\rm n,measd}^{\ \ a} \times 10^{-4}$	$M_{\rm w}/M_{\rm n}^{-d}$	$T_{g}^{e}(^{\circ}C)$
1	500	25	30	>99	98.7	3.41	3.69	1.03	45
2	1000	25	60	>99	98.7	6.81	9.63	1.04	45
3	2000	25	120	>99	98.2	13.6	24.1	1.07	46
4	3000	25	180	>99	98.2	20.4	35.4	1.07	43
5	4000	25	240	>99	98.1	27.2	42.7	1.08	47
6	5000	25	300	>99	98.1	34.1	49.2	1.09	42
7	500	0	120	94	99.3	3.21	3.95	1.03	48
8	500	40	20	>99	97.9	3.41	3.85	1.03	43
9	500	60	15	>99	97.7	3.41	4.02	1.03	40
10	500	80	10	>99	96.7	3.41	3.74	1.06	38
11^{f}	500	25	120	>99	98.7	3.41	3.79	1.04	39
12^g	500	25	240	90	98.7	3.01	4.63	1.06	39
13^h	500	25	30	>99	98.7	3.41	4.73	1.09	39
14^i	500	25	30	>99	98.7	3.41	5.76	1.04	39

^{*a*}Conditions: 1 10 μ mol, [Ph₃C][B(C₆F₅)₄] 10 μ mol, chlorobenzene 5 mL. ^{*b*}Determined by ¹H NMR and ¹³C NMR spectroscopy in CDCl₃. ^{*c*}Calculated by ([IP]/[Ln]) × 68.12 × yield. ^{*d*}Determined by GPC in THF at 40 °C against polystyrene standard. ^{*e*}Measured by DSC. ^{*f*}Toluene as the solvent. ^{*g*}Hexane as the solvent. ^{*h*}[PhNHMe₂][B(C₆F₅)₄] as the activator. ^{*i*}B(C₆F₅)₃ as the activator.



Figure 2. ¹³C NMR (CDCl₃) spectrum of 3,4-polyisoprene (99.3%; Table 1, entry 7).

noteworthy was that no matter what kind of organoborate $([(Ph_3C)(B(C_6F_5)_4)], [(PhNHMe_2)(B(C_6F_5)_4)], \text{ or } B(C_6F_5)_3)$ was used as the activator, the activity and selectivity of the IP polymerization were always unchanged. The ¹³C NMR spectrum revealed that the obtained PIP has medium 3,4-stereotacticity by giving the syndiotactic triad *rr* (45%) from δ 146.0 to 146.7 ppm and pentad *rrrr* (20%) at δ 146.7 ppm, respectively, while the signals between δ 147.0 and 148.3 ppm arise from the atactic 3,4-IP sequences and the weak resonance at δ 148.5 ppm is attributed to the isotactic triad *mm* (Figure 2). Such a microstructure endows the product high T_g (48 °C), as evidenced by DSC analysis (Figure S13, Supporting Information).

The kinetics study demonstrated that the conversion increased with polymerization time, and the number-average molecular weight (M_n) of the resulting polymer increased linearly with the conversion while the molecular weight distribution (M_w/M_n) remained almost unchanged (1.03–1.07), indicating that this binary system $1/[(Ph_3C)(B(C_6F_5)_4)]$ was among the few catalyst systems to date showing livingness characteristics for 3,4-selective polymerization of IP (Figure 3).^{21,25}

Block Copolymerization of Isoprene and ε -Caprolactone. The binary system $1/[(Ph_3C)(B(C_6F_5)_4)]$ could initiate the polymerization of ε -caprolactone (Table 2, entry 1). To our delight, the living lutetium-PIP active species could catalyze further ε -CL polymerization as the macroinitiator. In the ¹H NMR spectrum of the resultant PIP-b-PCL (Figure 4), the signals at δ 1.11–1.27 (m, -CH₂–), 1.53 (s, CH₃), 1.96 (s, CH), 4.57 (s, =CH₂), and 4.70 (s, =CH₂) arise from the PIP block and the tripletd at δ 4.06 (${}^{3}J_{H-H}$ = 6.7 Hz) and δ 2.31 $({}^{3}J_{H-H} = 7.5 \text{ Hz})$ and the multiplets at δ 1.65 and 1.38 are attributed to methylene protons of the PCL block. In order to prove the resulting polymer has a block microstructure rather than a mixture of the homopolymers, oligomeric PIP-b-PCL was prepared.³⁴ The ¹³C NMR spectrum of the oligomer gave two sets of signals arising from the PCL block: the strong signals at δ 173.53, 34.15, 24.61, 25.57, 28.39, and 64.16 ppm



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Figure 3. Polymerization of IP with $1/[(Ph_3C)(B(C_6F_5)_4)]$: molecular weight vs conversion ([Lu]₀ = 2.0 μ mol/mL, [IP]/[Lu] = 500, chlorobenzene, 25 °C).

are attributed to the repeating units $(-CO-(CH_2)_5-O-)$, while the weak signals at δ 173.73, 34.27, 24.75, 25.37, 28.55, and 62.56 ppm are derived from the terminal units (-CO- $(CH_2)_5$ -OH). A signal at δ 219.13 ppm is assignable to the ketone carbonyl connecting with the PIP sequence, -CH₂- $CH[C(CH_3)=CH_2]-CO-(CH_2)_5-O-$, the joint linkage of the two blocks, indicating that the resultant polymers are diblock copolymers (Figure S15, Supporting Information). The molecular weights of the resultant PIP-b-PCL copolymers increased proportionately with the monomer to Lu ratios, the molecular weight distribution remained narrow and unimodal (Figure 5), and the contents of the two blocks calculated by their integral intensities in the ¹H NMR spectrum were consistent with their loadings, which meant that the catalytic efficiency of the PIP-lutetium macroinitiators was very high and the copolymers were clean with a negligible presence of homopolymers. The thus medium syndiotactic 3,4-regulated PIP-b-PCL copolymers are unprecedented and cannot be accessed by the previously reported anionic living polymerization manner. The incorporation of a polar PCL block into a

Table 2. Copolymerization of Isoprene and ε -Caprolactone with $1/[Ph_3C][B(C_6F_5)_4]^a$



^{*a*}Conditions: Lu complex 10 μ mol, [Ph₃C][B(C₆F₅)₄] 10 μ mol, chlorobenzene/isoprene 10/1 (v/v), chlorobenzene/ ε -caprolactone 10/1 (v/v). ^{*b*}Polymerization time. ^{*c*}Determined by ¹H NMR and ¹³C NMR spectroscopy in CDCl₃. ^{*d*}Calculated by [([IP]/[Ln]) × 68.12 + [ε -CL]/[Ln] × 114.14] × yield. ^{*c*}Determined by GPC in THF at 40 °C against polystyrene standard.



Figure 4. ¹H NMR (CDCl₃) spectrum of PIP-*b*-PCL (Table 2, entry 3).



Figure 5. GPC traces of block copolymers of PIP-*b*-PCL (red) and the homopolymer PIP (blue) (Table 2, entry 3).

PIP macromolecular chain indeed aroused the change in the surface property such as the static water contact angle (WCA), which was measured by using the sessile drop method. The results showed that the WCA of the hydrophobic PIP (Table 1, entry 1) was 105.4° and the WCA of the hydrophilic PCL (Table 2, entry 1) was 82.9° , while a PIP-*b*-PCL block copolymer with an IP:CL ratio of 5:1 (Table 2, entry 2) gave a WCA of 98.6° between the two homopolymers (Figure S16, Supporting Information).

CONCLUSION

We have demonstrated that an amidino N-heterocyclic carbene ligand has been employed successfully to stabilize rare-earthmetal bis(alkyl) species, which provides a spacially bulky enough environment to the corresponding cationic active species generated upon activation of an organoborate, resulting in excellent activity and high 3,4-selectivity and livingness mode toward isoprene polymerization. The 3,4-selectivity of this system is nearly unaffected by the reaction temperature, monomer to catalyst ratio, and types of solvents and organoborates, suggesting a highly thermostable active species. In addition, the metal-3,4-polyisoprene active species could further initiate the copolymerization of the polar monomer ε -caprolactone to selectively afford unprecedented 3,4-PIP-*b*-PCL diblock copolymers.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified from the MBRAUN SPS system. LiCH2SiMe3 solution (1.0 M in pentane) was purchased from Aldrich. Glyoxal, mesitylamine, 2,6diisopropylphenylamine, 2-bromoethylamine hydrobromide, benzoyl chloride, thionyl chloride, and formaldehyde were purchased from the National Medicine Co. (People's Republic of China) and were used without further purification. Isoprene (99%, Acros) was dried over CaH_2 with stirring for 48 h and distilled before use. $^1\!H$ and $^{13}\!C$ NMR spectra were recorded on a Bruker AV400 instrument (FT: 400 MHz for ¹H, 100 MHz for ¹³C). Elemental analysis was performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). The number-average molecular weights $(M_{\rm n})$ and molecular weight distributions $(M_{\rm w}/M_{\rm n})$ of the polymer samples were measured by means of gel permeation chromatography (GPC) on a TOSOHHLC-8220GPC apparatus (column SuperHZM-Hx3) at 40 °C using THF as the eluent (the flow rate was 0.35 mL/ min) against polystyrene standards. Differential scanning calorimetry (DSC) analyses were carried out on a Q100 DSC from TA Instruments under a nitrogen atmosphere. The instrument was calibrated for temperature and enthalpy using pure indium (mp 156.6 °C) and sapphire before the experiments. Measurements during the first heating from 25 to 180 °C and then the first cooling from 180 to 25 °C as well as the second heating from 25 to 180 °C at 10 °C/ min were performed. Crystallographic data were collected at -86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector (Mo K, $\lambda = 0.71073$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The structures were solved by using the SHELXTL program. The static contact angle of the film was assessed by sessile drop angle measurement using a contact angle goniometer (DSA 100, Kruss GmbH, Hamburg, Germany) at 20 °C. At least five measurements were carried out for a single sample, and the values that were obtained were averaged. The testing liquid used was deionized water.

Synthesis of Amidino Imidazolium Bromide (AmH-NHC-H)Br. At room temperature, triethylamine (2.23 g, 22 mmol) in 20 mL of dichloromethane was added to a suspension of (NH₂CH₂CH₂(NCHCHN(C₆H₂Me₃-2,4,6)CH)Br)·HBr (3.91 g, 10 mmol) in 50 mL of dichloromethane and the mixture stirred 30 min. Then, C₆H₅C(Cl)N(C₆H₃ⁱPr₂-2,6) (3.00 g, 10 mmol) in 50 mL of dichloromethane was added dropwise to the solution and refluxed for 12 h. Removal of the volatiles under reduced pressure gave an offwhite residue that was washed three times with 500 mL of deionized water and then three times with 100 mL of ether and dried in vacuo to afford a white solid (4.5 g, 79%). ¹H NMR (400 MHz, CDCl₃, 7.26 ppm, 25 °C): δ 10.38 (s, 1H, imidazolium-H), 7.68 (s, 1H, NCH), 7.25–7.17 (m, 5H, C_6H_5), 7.00 (s, 2H, $C_6H_2Me_3$), 6.97–6.89 (m, 3H, 2,6- $Pr_2C_6H_3$), 6.39 (s, 1H, NCH), 5.13 (t, ${}^3J_{H-H} = 5.6$ Hz, 2H, CH₂CH₂), 4.27 (s, 2H, CH₂CH₂), 2.89 (sept, 2H, CH(CH₃)₂), 2.35 (s, 3H, $C_6H_2Me_3$), 2.03 (s, 6H, $C_6H_2Me_3$), 1.28 (d, ${}^3J_{H-H} = 6.8$ Hz, 6H, CH(CH₃)₂), 0.85 (d, ${}^3J_{H-H} = 6.8$ Hz, 6H, CH(CH₃)₂). ${}^{13}C$ NMR (100 MHz, C_6D_6 , 25 °C): δ 17.40 (s, 2C, $C_6H_2Me_3$), 20.94 (s, 1C, C₆H₂Me₃), 22.05 (s, 2C, CH(CH₃)₂), 24.04 (s, 2C, CH(CH₃)₂), 28.07 (s, 2C, CH(CH₃)₂), 41.60 (s, 1C, CH₂CH₂), 48.58 (s, 1C, CH₂CH₂), 130.49 (s, 1C, NCH), 128.25 (s, 1C, NCH), 138.33 (s, 1C, imidazolium-CH), 121.65, 122.04, 122.68, 127.28, 127.89, 128.84, 129.68, 133.12, 134.05, 137.58, 141.14, 145.24 (m, ArC), 157.58 (s, 1C, NCN). Anal. Calcd for C₃₃H₄₁N₄Br: C, 69.10; H, 7.20; N, 9.77. Found: C, 69.49; H, 7.35; N, 9.52.

Synthesis of the Complex (Am-NHC)Lu(CH_2SiMe_3)₂ (1). Under a nitrogen atmosphere, Li CH_2SiMe_3 (0.047 g, 0.5 mmol) in 0.5 mL of pentane was added to a suspension of (AmH-NHC-H)Br (0.287 g, 0.5 mmol) in 5 mL of toluene and the mixture stirred for 20 min. Then, the suspension was added to a solution of Lu- $(CH_2SiMe_3)_3(THF)_2$ (0.290 g, 0.5 mmol) in 5 mL of toluene. The reaction was maintained for another 2 h, and then the solution was concentrated until it became cloudy. The LiBr precipitate was filtered off. The filtrate was concentrated and then cooled to -30 °C. Colorless crystalline complex 1 was isolated within 2 days (0.528 g, 62.9%). ¹H NMR (400 MHz, C_6D_{67} 25 °C): δ -0.85, -0.82 (AB, ${}^{2}J_{H-H} = 11.2$ Hz, 2H, Lu-CH₂SiMe₃), -0.65, -0.62 (AB, ${}^{2}J_{H-H} = 11.2$ Hz, 2H, Lu-CH₂SiMe₃), 0.19 (s, 18H, Lu-CH₂SiMe₃), 1.13 (d, ${}^{3}J_{H-H} =$ 6.8 Hz, 6H, CH(CH₃)₂), 1.50 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 6H, CH(CH₃)₂), 2.02 (s, 6H, C₆H₂Me₃), 2.20 (s, 3H, C₆H₂Me₃), 3.19-3.21 (m, 2H, CH₂CH₂), 3.57–3.59 (m, 2H, CH₂CH₂), 3.71 (sept, 2H, CH(CH₃)₂), 5.95 (d, ${}^{3}J_{H-H} = 1.6$ Hz, 1H, NCH), 6.01 (d, ${}^{3}J_{H-H} = 1.6$ Hz, 1H, NCH), 6.83–6.86 (m, 3H, 2,6– $Pr_2C_6H_3$), 6.89–6.93 (m, 2H, C₆H₂Me₃), 6.95–7.06 (m, 5H, C₆H₅). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ 4.65 (s, 6C, Lu-CH₂SiMe₃), 18.15 (s, 2C, C₆H₂Me₃), 21.07 (s, 1C, C₆H₂Me₃), 24.13 (s, 2C, CH(CH₃)₂), 26.51 (s, 2C, CH(CH₃)₂), 28.16 (s, 2C, CH(CH₃)₂), 46.72 (s, 2C, Lu-CH₂SiMe₃), 48.41 (s, 1C, CH₂CH₂), 54.55 (s, 1C, CH₂CH₂), 120.38 (s, 1C, NCH), 121.67 (s, 1C, NCH), 123.66, 124.54, 127.94, 129.11, 129.32, 129.81, 133.02, 135.26, 136.56, 139.45, 142.87, 143.25 (m, ArC), 176.77 (s, 1C, NCN), 199.66 (s, 1C, Lu-C_{vlidene}). Anal. Calcd for C41H61LuN4Si2: C, 58.55; H, 7.32; N, 6.66. Found: C, 58.93; H, 7.52; N, 6.47.

Isoprene Polymerization. A typical polymerization procedure (Table 1, entry 1) was as follows. Under a nitrogen atmosphere, a chlorobenzene solution (2.5 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μ mol) was added to a well-stirred chlorobenzene solution (2.5 mL) of complex 1 (8.4 mg, 10 μ mol) in a flask. The reaction apparatus was placed in a bath at 25 °C. Then 0.5 mL of isoprene (0.34 g, 5 mmol) was added to the above system to start the polymerization and stirring was maintained for 30 min; the viscous reaction solution was poured into ethanol (ca .30 mL) to terminate the polymerization. The PIP product was precipitated, filtered, washed with ethanol, and dried under vacuum at 40 °C to a constant weight (0.34 g, 100%). The isolated PIP has a 98.7% 3,4-tacticity and a number-average molecular weight of 3.69×10^4 with a molecular weight distribution of 1.03. The glass transition temperature is 45 °C. ¹H NMR (400 MHz, CDCl₃, 25 ^oC): δ 1.11–1.27 (m, 2H, -CH₂–), 1.53 (s, 3H, CH₃), 1.96 (s, 1H, CH), 4.57 (s, 1H, =CH₂), 4.70 (s, 1H, =CH₂). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 17.68–18.29 (m, 1C, CH₃), 36.75–39.87 (m, 1C, -CH₂-), 41.85-42.20 (m, 1C, -CH-), 111.42-112.63 (m, 1C, $=CH_2$), 146.30-147.82 (m, 1C, $C(CH_3)=CH_2$).

Copolymerization of Isoprene and ε -Caprolactone with 1/ $[Ph_3C][B(C_6F_5)_4]$. A typical polymerization procedure (Table 2, entry 3) was as follows. Under a nitrogen atmosphere, a chlorobenzene solution (2.5 mL) of $[Ph_3C][B(C_6F_5)_4]$ (9.2 mg, 10 μ mol) was added to a well-stirred chlorobenzene solution (2.5 mL) of complex 1 (8.4 mg, 10 μ mol) in a flask. The reaction apparatus was placed in a bath at 25 °C. Then 0.5 mL of isoprene (0.34 g, 5 mmol) was added to the above system to start the polymerization. After 30 min, a small amount of polymer solution was taken to terminate the polymerization. Then a chlorobenzene solution (5 mL) of *e*-caprolactone (0.57 g, 5 mmol) was added to the above system and the polymerization was continued for another 120 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 (0.81 g, 100%). $^1\!\mathrm{H}$ NMR (400 MHz, CDCl₃, 25 °C): δ 1.11-1.27 (m, 2H, -CHCH₂-), 1.38 (m, 2H, $-(CH_2)_2CH_2(CH_2)_2-$), 1.53 (s, 3H, -CH ($CH_3=CH_2$), 1.65 (m, 4H, -CH₂CH₂CH₂CH₂CH₂-), 1.96 (s, 1H, -CHCH₂-), 2.31 (t, ${}^{3}J_{H-H}$ = 7.5 Hz, 2H, -COCH₂-), 4.06 (t, ${}^{3}J_{H-H}$ = 6.7 Hz, 2H, -CH₂O-), 4.57 (s, 1H, -CH=CH₂), 4.70 (s, 1H, -CH=CH₂). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 17.68-18.29 (m, 1C, -CH(CH₃)), 24.66 (s, 1C, -COCH₂CH₂-), 25.61 (s, 1C, $-(CH_2)_2CH_2(CH_2)_2-$), 28.43 (s, 1C, $-CH_2CH_2O-$), 34.20 (s, 1C, -COCH₂-), 36.75-39.87 (m, 1C, -CHCH₂-), 41.85-42.20 (m, 1C, -CHCH₂-), 64.21 (s, 1C, -OCH₂-), 111.42-112.63 (m,

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 $1C_{7}-CH = CH_{2}$), 146.30–147.82 (m, 1C, $-C(CH_{3})=CH_{2}$). 173.59 (s, 1C, -CO-).

ASSOCIATED CONTENT

S Supporting Information

Figures, a table, and a CIF file giving characterization data for 1 and the polymers, contact angles of the polymers PIP, PCL and PIP-*b*-PCL, and crystallographic data for 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(34) ¹H NMR (400 MHz, CDCl₃, 25 °C) of the oligomer of homopolyisoprenes: δ 4.70 (1H, CH₂==C, 3,4-PIP), 4.57 (1H, CH₂==C, 3,4-PIP), 1.96 (1H, CH, 3,4-PIP), 1.53 (3H, CH₃, 3,4-PIP), 1.19 (2H, CH₂, 3,4-PIP), 0.36 (0.05H, CH₂Si(CH₃)₃), -0.04 (0.24H, CH₂Si(CH₃)₃). The molecular weight (M_n) is 2700. ¹H NMR (400 MHz, CDCl₃, 25 °C) of the oligomer of the copolymers PIP-*b*-PCL: δ 4.70 (1H, CH₂==C, 3,4-PIP), 4.57 (1H, CH₂==C, 3,4-PIP), 4.66 (1.8H, CH₂, PCL), 3.64 (0.06H, -CH₂OH), 2.31 (1.8H, CH₂, PCL), 1.96 (1H, CH, 3,4-PIP), 1.65 (3.7H, CH₂, PCL), 1.53 (3H, CH₃, 3,4-PIP), 1.38 (1.8H, CH₂, PCL), 1.19 (2H, CH₂, 3,4-PIP), 0.36 (0.05H, CH₂Si(CH₃)₃), -0.04 (0.24H, CH₂Si(CH₃)₃). The molecular weight (M_n) is 5800. For the ¹³C NMR spectrum of oligomeric copolymers PIP-*b*-PCL, see Figure S15 in the Supporting Information.