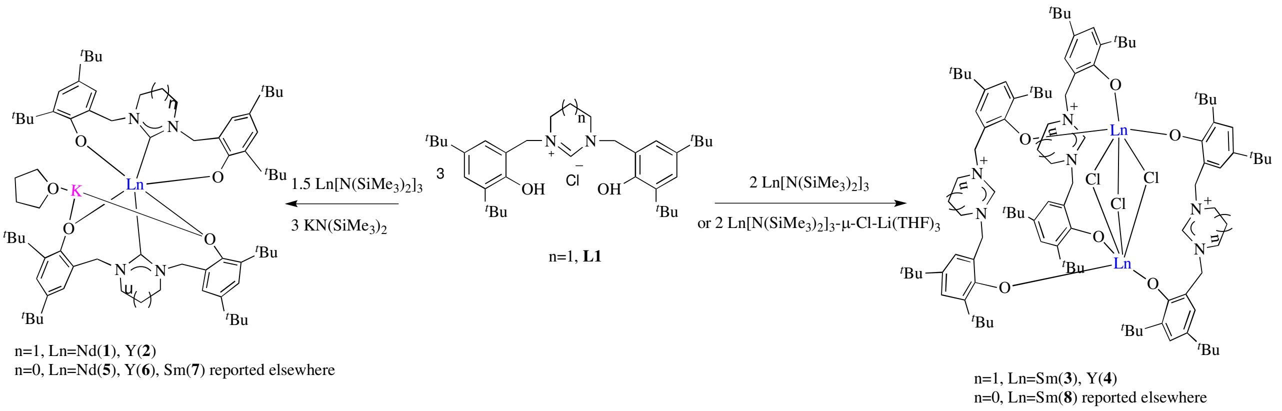
RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances



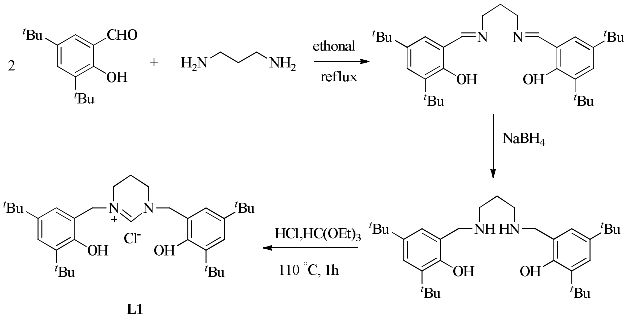
Scheme 2 Synthesis of NHC rare earth metal complexes **1**-**4**.

Here we report the synthesis and characterization of pyrimidinium based N-heterocyclic carbene rare earth metal complexes as well as the comparison of activities with imidazolinium based NHC counterparts toward the polymerization of *n*-hexyl isocyanate. The mechanism of the initiation step of the polymerization was also studied by NMR analysis.

Results and discussion

Synthesis and characterization of complexes 1-4

The ligand used in this work was designed and synthesized easily. N,N'-bis(3,5-di-tert-2-hydroxyphenylmethyl)propylenediimine was obtained by the reaction of 3,5-di-*tert*-butylsalicylaldehyde with 1,2-propanediamine in ethanol at reflux temperature, and then reduced by NaBH$_4$ to give the corresponding diamine.[14] Finally, the bis(phenolate) NHC precursor, N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenylmethyl)pyrimidinium chloride (**L1**) was synthesized by treatment of diamine with HCl and CH(OEt)$_3$ at reflux temperature (Scheme 1).



Scheme 1 Synthesis of **L1**

Complex **1** was synthesized by treatment of **L1** with 1 equiv of KN(SiMe$_3$)$_2$ and half equiv of Nd[N(SiMe$_3$)$_2$] in THF at -30°C (Scheme 2). The ORTEP diagram is depicted in Fig. 1 with the selected bond lengths and angles. The ligand coordinates to Nd in a tridentate mode, with two oxygens on the aryloxo groups and C$_{carbene}$ on the six-membered ring.

The geometry of the potassium atom is planar with two oxygens on one ligand and one oxygen on THF molecule. The central metal Nd is six-coordinated by the geometry of distorted octahedron, with O1, O2, O4 and C45 (linking to N3 and N4) occupying the equatorial positions and O3, C11 occupying the axial positions of the octahedron. The similar structure of imidazolinium based NHC complexes has been reported by us and here we employ the complexes for comparison (Scheme 2, complexes **5**-**8**).[5j] The average bond length of Nd-C$_{carbene}$ 2.759 Å falls in the range of the published literatures,[5g, 5h, 5j, 15] slightly longer than that of the imidazolinium based NHC Nd complex (2.716 Å). The bond angle of N-C$_{carbene}$-N increases from 107.2° of imidazolinium based NHC to 116.3° of pyrimidinium based NHC complex **1**.

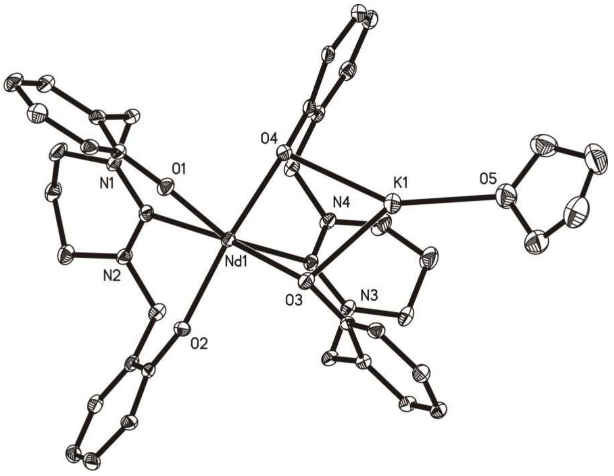


Fig. 1 X-ray structure of complex **1**, with 30% probability thermal ellipsoids. Hydrogen atoms and *tert*-butyl groups are omitted for clarity.Selected bond distances (Å) and angles (°) of **1**: Nd1-O1 2.226(2), Nd1-O2 2.267(2), Nd1-O3 2.315(2), Nd1-O4 2.339(2), Nd1-C11 2.750(4), Nd1-C45 2.767(3), K1-O3 2.727(2), K1-O4 2.766(2), K1-O5 2.696(3), N1-C11 1.346(4), N2-C11 1.335(4); O1-Nd1-O2 102.87(8), O3-Nd1-O4 89.20(8), C11-Nd1-C45 88.99(10), O1-Nd1-C11 82.06(9), O2-Nd1-C11 80.13(9), O3-Nd1-C45 77.43(9), O4-Nd1-C45 73.23(9), O3-K1-O4 73.01(7), O3-K1-O5 128.47(8), O4-K1-O5 151.82(8), N1-C11-N2 116.3(3)

The average bond length of the Nd-O on the ligand which the oxygens link to the potassium atom is 2.326 Å, longer than the Nd-O distance (2.246 Å) on the other ligand. The average bond length of K-O is 2.729 Å. The tridentate ligand bends to half a circle when coordinated to the metal center and the ligand without the binding force of potassium opens wider with the bond angle of O1-Nd1-O2 at 102.9° in contrast with the 89.2° of O3-Nd-O4.

Complex **2** was synthesized in a similar way. Suitable crystals for X-ray diffraction were not obtained. NMR analysis could not be performed on Nd complex **1** due to the paramagnetic properties and complex **2** was characterized by ^{1}H(^{13}C) NMR analysis. The chemical shift of the ^{1}H NMR spectrum moved downfield towards the ligand with potassium ion due to the electron-withdrawing effect of the alkali metals. The methene hydrogen [CH_2-Ar] linking the phenyl ring on the ligand with potassium ion showed high chemical shift at δ 5.4-6.3 in comparison with that of δ 2.8-3.8 the counterpart at the other ligand. The formation of Y-C$_{\mathrm{carbene}}$ bond could be observed obviously by ^{1}H(^{13}C) NMR spectra. The resonance of the hydrogen on the six-membered ring (C2) was at δ 8.72 in $CDCl_3$ and the resonance peak diminished after deprotonation by $KN(SiMe_3)_2$ and coordination with yttrium. The high C$_{\mathrm{carbene}}$ resonance appeared at δ 211.37 and 211.99. Complexes **1**-**2** were soluble in THF and toluene and partially soluble in hexane.

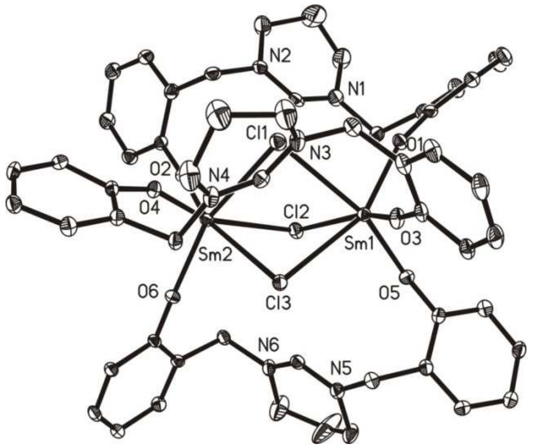


Fig. 2 X-ray structure of complex **3**, with 30% probability thermal ellipsoids. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond distances (Å) and angles (°) of **3**: Sm1-O3 2.183(3), Sm1-O5 2.199(3), Sm1-O1 2.199(3), Sm1-Cl1 2.851(11), Sm1-Cl2 2.858(11), Sm1-Cl3 2.872(11), N1-C11 1.312(6), N2-C11 1.306(6), O3-Sm1-O5 102.86(11), O3-Sm1-O1 101.60(11), O5-Sm1-O1 104.59(11), O3-Sm1-Cl1 96.70(8), O5-Sm1-Cl1 157.89(8), O1-Sm1-Cl1 81.13(8), O3-Sm1-Cl2 158.49(9), O5-Sm1-Cl2 81.38(8), O1-Sm1-Cl2 97.58(8), Cl1-Sm1-Cl2 76.66(3), O3-Sm1-Cl3 83.02(9), O5-Sm1-Cl3 96.38(8), O1-Sm1-Cl3 156.76(8), Cl1-Sm1-Cl3 75.70(3), Cl2-Sm1-Cl3 75.53(3), Sm2-Cl1-Sm1 89.80(3), Sm2-Cl2-Sm1 89.52(3), Sm1-Cl3-Sm2 88.80(3), N2-C11-N1 124.7(4).

Complex **3** was synthesized by treatment of a stirring solution of **L1** with $Sm[N(SiMe_3)_2]_3$ or $Sm[N(SiMe_3)_2]_3$-μ-Cl-Li$(THF)_3$ in THF at room temperature for 1 day. Complex **3** was soluble in THF and had a poor solubility in toluene and hexane. Without the addition of strong base $KN(SiMe_3)_2$, the hydrogen on the NHC ring of the NHC precusor could not be abstracted. The two Sm metal centers were also bridged by the three chloride ions from the ligand and forming the pyrimidinium-bridged rare earth metal complex. The solid structures of complex **3** were detected by single-crystal X-ray diffraction analysis. ORTEP drawing, bond lengths and angles are compiled in Fig. 2. Three ligands coordinate to two metal centers in a bidentate mode. The geometry at the metal center Sm is best described as a trigonal antiprism, with three oxygens from the three ligands on one plane and three chlorides on the other plane. On the bridged six-membered ring, the bond angle of N1-C11-N2 is 124.7°, larger than the 116.3° of complex **1**, and larger than the 114.7° of imidazolinium based NHC complex **5**. In complex **3**, the bond angles of Sm1-Cl-Sm2 are between 88.8-89.8°, slightly smaller than the 90.9-91.6° in imidazolinium based NHC Sm complex **8**;[5j] the sum of Cl-Sm1-Cl is 227.9°, larger than that of 223.9° in complex and shows a more contact structure in complex **3**. The hydrogens (NC*H*N, NC*H*H-Ar) have some interactions with chlorides. C-H···Cl hydrogen bond lengths ranges from 2.64 to 2.83 Å with the bond angles of C-H···Cl ranges from 137.6 to 158.1° in the solid structure, showing some characteristics of the C−H···Cl interactions.[16] Complex **4** was synthesized by the same method with complex **3**, using $Y[N(SiMe_3)_2]_3$ instead. ^{1}H(^{13}C) NMR analysis was performed on complex **4** in THF-d$_8$. The ^{1}H NMR spectrum shows that the resonances of a half hydrogens on the methene (NC*H*H-Ar) occur at δ 6.47, 6.50 due to the C-H···Cl interaction, and the methine H on the ring (NC*H*N) occurs at δ 9.63. The resonance of the other half hydrogens on the methene (NCH*H*-Ar) which do not participate in the C-H···Cl interaction occur at δ 3.57, 3.59. The ^{13}C NMR spectrum shows that the resonance of the methine carbon (N*C*HN) occurs at δ 153.41.

All the complexes are air and moisture sensitive.

Polymerization of *n*-hexyl isocyanate

The relationship of structure and catalytic activity of these rare earth metal complexes were studied and the polymerization data were listed in Table 1. All of the polyisocyanates obtained showed very high molecular weight (up to 10^6) with narrow molecular weight distribution (M_w/M_n = 1.7-2.3) when using toluene as the solvent and the yield could exceed 60%. The pyrimidinium based NHC rare earth complexes **1**-**2** and imidazolinium based NHC rare earth complexes **5**-**7** exhibited high activities toward the polymerization of *n*-hexyl isocyanate in comparatively mild conditions compared with that of the anionic polymerizations. However, non-NHC rare earth complexes **3**, **4**, **8** showed no activity, which probably suggested the NHC moiety played an important role in the polymerization. The polymerization rate was very fast with considerable viscosity of the solution upon the addition of the catalyst. Thus, adequate toluene solvent was considered to slow down the polymerization process for the sake of a well dispersion of the complexes in the polymerization system as well as a better control of the polymerization and an easier comparison of the structure and activity among the complexes. Complex **5** was employed to optimize the polymerization condition of *n*-hexyl isocyanate. Polymerization temperature exerted great influence on the activity and lower temperature facilitated the polymerization with -20 °C giving the highest polymerization yield (entry 11). Polymerization of *n*-hexyl isocyanate could be performed at 0 °C with relatively low yield as was observed in entry 9.

Table 1 Polymerization of *n*-hexyl isocyanate catalyzed by complex **1**-**2**, **5**-**7**[a]

Entry	Complex	$[I]_0/[M]_0$	Temp.(°C)	*t* (min)	yield[b]	10^{-4} *Mn*[c]	M_w/M_n[c]
1	**1**	1:700	-20	1	28	58	2.21
2	**1**	1:700	-20	5	57	59	2.20
3	**1**	1:700	-20	10	60	62	2.21
4	**1**	1:700	-20	30	64	69	2.23
5[d]	**1**	1:700	-20	30	63	49	2.32
6[e]	**1**	1:700	-20	15	9	35	2.50
7	**2**	1:700	-20	360	8	97	1.91
8[d]	**2**	1:700	-20	5	15	83	1.85
9	**5**	1:700	0	30	18	80	1.80
10	**5**	1:700	-10	30	45	92	1.76
11	**5**	1:700	-20	30	64	99	1.72
12	**5**	1:700	-30	30	59	97	1.71
13	**5**	1:700	-20	5	33	74	1.84
14	**5**	1:700	-20	15	48	98	1.71
15	**5**	1:700	-20	120	60	98	1.77
16	**5**	1:500	-20	30	63	78	1.89
17	**5**	1:1000	-20	30	41	106	1.84
18	**6**	1:700	-20	120	10	93	1.84
19	**6**	1:700	-20	360	18	92	1.90
20	**7**	1:700	-20	30	34	102	1.80
21	**7**	1:700	-20	60	59	101	1.78
22	**7**	1:700	-20	120	62	97	1.83

[a]General polymerization conditons: toluene as the solvent, [*n*-hexyl isocyanate] = 1 M. . [b]Yield: (weight of polymer obtained)/(weight of monomer used). [c]Measured by GPC relative to polystyrene standards. [d][*n*-hexyl isocyanate] = 10 M, toluene as the solvent. [e]Polymerized in THF.

The polymerization of isocyanate displayed celling temperature effects and monomer to trimer transformation might exist which decreased the yield.[7d] The monomer/complex ratio could rise to 1000 with the yield exceeding 40% (entry 17). The polymerization yield could reach 57% in 5 minutes catalyzed by the pyrimidinium based NHC complex **1** (entry 2), exhibiting a higher catalytic activity than the imidazolinium based one which might indicate the higher activity of the pyrimidinium based NHC and the easier breakage of the rare earth metal carbene bond. However, the polymers obtained by complex **1** gave lower molecular weights and comparatively wider molecular weight distributions. The activity of the polymerization decreased greatly using the polar solvent THF instead which could be reasonably explained by the completion of the THF molecule with monomer for coordination at the high oxophilic affinitive metal center (entry 6).[17]

The catalytic activities of the yttrium complexes were obviously decreased due to the steric effect caused by the much smaller radius of the metal and the pyrimidinium based NHC showed much steric hindrance and reduced the activity. However, the yield could reach 15% in 5 minutes in a higher monomer concentration catalyzed by the yttrium complex **2** (entry 8). For the imidazolinium based NHC Sm complex, the catalytic activity was high but lower than that of complex **5**. The yield could exceed 60% within 2 hours by both Nd complexes and small radius Sm complex. The magnitude of the activity of different rare earth metal complexes was in line with the radius of the rare earth metal (Nd > Sm > Y). Complexes with suitable metal radius provided enough room for the coordination of the monomers at the metal center.

Previously, lanthanum isopropoxide[7a] and phenolate rare earth metal complexes[18] were found active for the polymerization of *n*-hexyl isocyanate. Surprised by the inactivity of the bis(phenolate) non-NHC rare earth metal complexes toward the polymerization of *n*-hexyl isocyanate which suggested the Ln-O bond could not catalyze the polymerization, we further researched the mechanism of the initiation of polymerization by the NHC complexes. The initiation step of the polymerization by the NHC complex **2** was monitored by NMR analysis. The ^{1}H NMR spectrum was shown in Fig. 3 and the ligand with potassium ion was omitted for clarity. The electron-withdrawing effect of potassium ion could be seen by chemical shifts of hydrogen on the ligands, so the potassium ion linked to the second ligand all the time. The function of NHC moiety in the initiation was observed by the in situ ^{1}H NMR analysis in abstracting the one hydrogen after the bond breakage of the yttrium-NHC. The most striking evidence of the hydrogen abstraction of NHC was the hydrogen H^a found at δ 8.78 on the ^{1}H NMR spectrum. Meanwhile, the high resonance of the $C_{carbene}$ that was supposed to appear at δ 211.68 and 216.89 in toluene-d_8 disappeared on the ^{13}C NMR spectrum (Fig. s11). This pattern of initiation was rare, but can also be found in the initiation of L-Lactide polymerization by the imidazolinium based NHC complexes **5**-**7** in which the free NHC abstracted the methine hydrogen of L-Lactide.[5j] For the convenience of judgment of the signals of the hydrogen and carbon on the spectra, two online ^{1}H(^{13}C) NMR spectra were performed with one of complex nearly all participated in the initiation and the other of complex a small amount participated. The two-dimensional NMR spectra ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC were also performed on the polymerization system with a small amount of complex participated in the initiation (Fig. 4 and see supporting info, Fig.s12-14).

N-hexyl isocyanate was thought to provide the hydrogen resource. After hydrogen-abstraction, the hydrogen left H^i on the chiral carbon occurred at δ 4.27, 4.02 and the methene signals were coupled with protons H^j (δ 1.97) on adjacent carbon (Fig. 4). The signals of the chiral carbon on the ^{13}C NMR spectrum were at δ 45.62, 44.87 (see details of comparison in supporting info, Fig. s 10-11 and ^{1}H-^{13}C HSQC Fig. s14). The signal at δ 3.25 was assigned to H^k, which was coupled with H^t and H^j on the ^{1}H-^{1}H COSY spectrum. The proposed mechanism was shown in Scheme 3, and the second ligand with potassium ion of the complex was omitted for clarity. The integration of abstracted hydrogen is in proportion (1:4) to that of the hydrogen on the phenyl, so both the ligands participated in the initiation. After abstraction, the carbanion was thought to be the initiating species in the polymerization ~~by the monomer coordination-insertion anionic mechanism~~. The polymerization was terminated by adding excess methanol.

Small amount of *n*-hexyl isocyanate was found compared with the ^{1}H NMR spectrum of the *n*-hexyl isocyanate in toluene-d_8 (see supporting info, Fig. s7). The conversion of *n*-hexyl isocyanate to cyclic trimer as a result of back-biting reaction was thought to decrease the yield of polymerization. A large amount of trimers existed in this system.[13h, 19] Some remaining unreacted NHC yttrium complex existed in this system and could be identified.

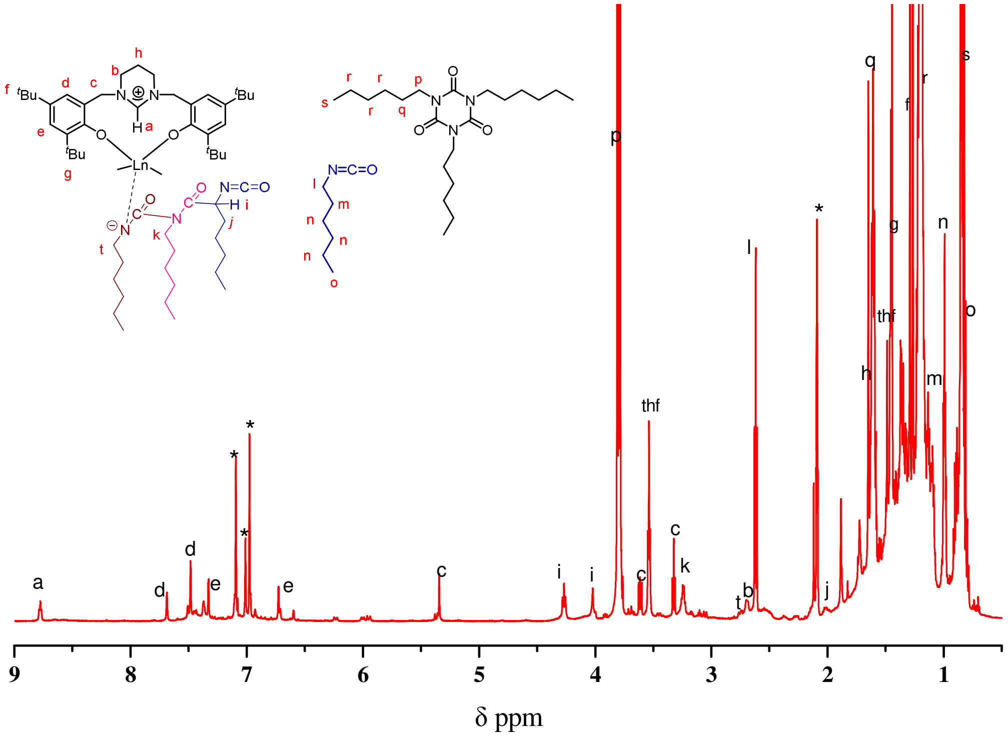
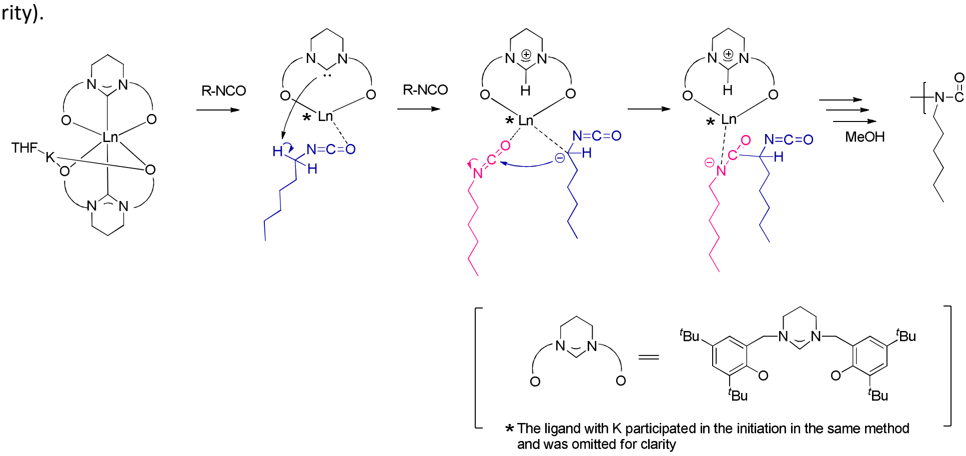


Fig. 3 ^{1}H NMR spectrum of in situ polymerization of *n*-hexyl isocyanate initiated by complex **2** in toluene-d_8 (*toluene, the ligand with K was omitted for clarity).



* The ligand with K participated in the initiation in the same method and was omitted for clarity

Scheme 3 The proposed mechanism of the initiation by NHC rare earth metal complexes

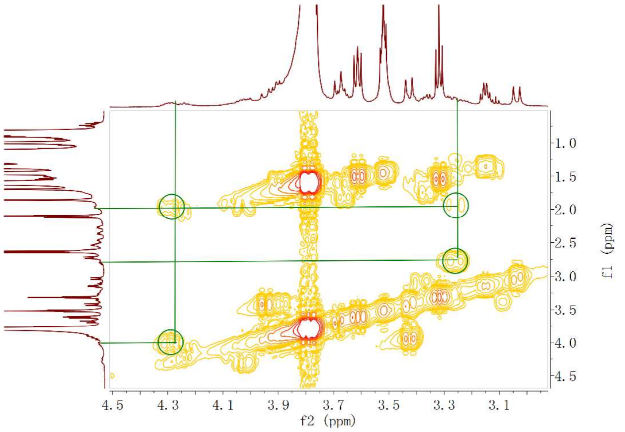


Fig. 4 ^{1}H-^{1}H COSY spectrum of in situ polymerization of *n*-hexyl isocyanate initiated by complex **2** in toluene-*d*$_8$.

Conclusions

The bis(phenolate) pyrimidinium based NHC rare earth metal complexes and bis(phenolate) pyrimidinium-bridged rare earth metal complexes were successfully synthesized and characterized by X-ray diffraction analysis, ^{1}H(^{13}C) NMR analysis and elemental analysis. The imidazolinium and pyrimidinium based NHC rare earth metal complexes had been applied in the polymerization of *n*-hexyl isocyanate. The polymer obtained showed very high molecular weight and narrow molecular weight distribution. The catalytic activity was much affected by the radius of rare earth metal, solvent, polymerization temperature and the structure of the ligand. The pyrimidinium-bridged rare earth metal complexes were inactivity for the polymerization. The mechanism of the initiation by NHC rare earth metal complexes was studied, and NHC moiety played an important role in the initiation step, which was evidenced by NMR analysis. ~~A monomer coordination-insertion anionic polymerization mechanism was proposed based on the hydrogen abstraction initiation.~~

Experimental Section

General Procedures.

The syntheses of rare earth metal complexes and polymerization were carried out under purified argon atmosphere using Schlenk techniques. Hexane, THF and toluene were distilled from sodium benzophenone ketyl before use. All other reagents and solvents were commercially available. HN(TMS)$_2$ was dried over CaH$_2$ and distilled under vacuum. *n*-Hexyl isocyanate was dried over CaH$_2$ and distilled under vacuum over three times. Metal analyses were performed by complexometric titration. NMR spectra were recorded on an Agilent 600MHz Direct Drive 2 spectrometer. Elemental analyses were performed by direct combustion with a Flash EA-1112 instrument. Molecular weight and molecular weight distribution were measured by GPC equipped with a RI (Waters 2414) detector and a Waters 1525 isocratic high performance liquid chromatography pump at 40 °C with THF as the eluent at a flow rate of 1.0 mL min^{-1}. The starting materials of Ln[N(SiMe$_3$)$_2$]$_3$-μ-Cl-Li(THF)$_3$[20] and Ln[N(SiMe$_3$)$_2$]$_3$[21] were synthesized according to literature procedures. The yttrium complexes samples for NMR analysis were prepared in a glovebox using dry and oxygen-free NMR tubes. The in situ reaction of complex **2** and *n*-hexyl isocyanate were performed at -20°C for several minutes in toluene-*d*$_8$ sealed in dry and oxygen-free NMR tubes and measured on Agilent 600MHz Direct Drive 2 spectrometer at room temperature.

Synthesis of L1. 1,2-propanediamine (1.65ml) in ethanol was dropped in the ethanol solution of 3,5-di-*tert*-butylsalicylaldehyde (9g) at reflux temperature for 2h, then reduced by NaBH$_4$ (5.8g), adding 50ml THF and reflux overnight. The solution was evaporated under vacuum and washed by water and extracted by CH$_2$Cl$_2$.after evaporation, the resultant recrystallized in ethanol/ethyl acetate mixture for twice. The white solid (4.95g, 10mmol) was dissolved in ethanol/EtOAc and was treated with concentrate HCl (2.2ml, 22mol) for half an hour. After evaporation, the white solid was reacted with HC(OEt)$_3$ (50ml) and HCOOH (9 drops) at 120°C for 1h. White precipitation (3g) was formed and filtrated. The precipitation was washed with ethyl ether three times. ^{1}H NMR (600MHz, CDCl$_3$) δ 8.86 (1H, s, C2-H(imid)), 7.32 (2H, d, Ar-H), 6.93(2H, d, Ar-H), 4.85(4H, s, CH$_2$), 3.26(4H, t, NC*H*$_2$CH$_3$C*H*$_2$N), 1.99(2H, q, NCH$_3$C*H*$_2$CH$_3$N) 1.42(18H, s, tBu),1.26(18H, s, tBu); ^{13}C NMR (600MHz, CDCl$_3$) δ 19.02(NCH$_2$*C*H$_2$CH$_2$N); 30.35(-C(*C*H$_3$)$_3$); 31.71(-C(*C*H$_3$)$_3$); 34.38(-*C*(CH$_3$)$_3$); 35.27(-*C*(CH$_3$)$_3$); 42.25(N*C*H$_2$CH$_2$*C*H$_2$N); 56.83(N*C*H$_2$-Ar); 122.01(tBu-Ar); 125.33(tBu-Ar); 125.77(CH$_2$-Ar); 140.72(H-Ar); 143.29(H-Ar); 152.76(N*C*HN); 153.59(O-Ar).

Synthesis of L1$_2$NdK(THF)(1). In a THF solution, **L1** (0.37mmol) was reacted with Nd[N(SiMe$_3$)$_2$]$_3$ (0.18mmol) and KN(SiMe$_3$)$_2$ (1.11mol) and stirred for 2h at -30°C and overnight at room temperature. Then solvent was removed under vacuum and extracted by hexane/THF solvent mixture. Blue block crystals were obtained at room temperature in 1-2 days. Anal. Calcd for $C_{72}H_{108}N_4O_5NdK$: C, 66.90; H, 8.26; N, 4.59. Found: C, 67.18; H, 8.59; N, 4.47.

Synthesis of L1$_2$YK(thf)(2). Following a similar procedure described for complex 1. Treatment of a stirring solution of **L3** (0.20g, 0.37mmol) in THF with Y[N(SiMe$_3$)$_2$]$_3$ (0.18mmol) and KN(SiMe$_3$)$_2$ (1.11mol). The reaction mixture was stirred for 2h at -30°C and overnight at room temperature, and then the solvent was removed under vacuum and extracted by hexane/THF solvent mixture. Colorless crystals were obtained at room temperature in 1-2 days. ^{1}H NMR (600M, C$_6$D$_6$) δ 1.37, 1.38, 1.50 (36H, s , tBu); 1.52,1.55, 1.78, 1.97(36H, s , tBu); 1.40(4H, t , THF); 1.74(4H, s, NCH$_2$C*H*$_2$CH$_2$N); 2.28, 2.35, 2.42, 2.53, 2.70(8H, m, NC*H*$_2$CH$_2$C*H*$_2$N); 2.84, 3.14, 3.47, 3.75, 5.46, 6.05, 6.07, 6.26(8H, b, NCH$_2$-Ar); 3.52(4H, m, THF); 6.70, 6.84, 6.95, 7.17(4H, b, Ar-H); 7.44, 7.60(4H, m, Ar-H); ^{13}C NMR (600M, C$_6$D$_6$) δ 25.81(THF); 19.86, 21.44(NCH$_2$*C*H$_2$CH$_2$N); 31.06, 31.15, 31.48, 31.56 (-C(*C*H$_3$)$_3$); 32.14, 32.20, 32.50, 32.52(-C(*C*H$_3$)$_3$); 34.05, 34.09, 34.16, 34.23(-*C*(CH$_3$)$_3$); 35.71, 35.73, 36.20, 36.24(-*C*(CH$_3$)$_3$); 39.87, 40.03, 40.54, 40.65(N*C*H$_2$CH2*C*H$_2$N); 60.14, 61.01, 61.69, 62.01(N*C*H$_2$-Ar); 67.79(THF); 123.06, 123.74, 123.93, 124.43(tBu-Ar); 124.93, 125.13, 125.30, 125.46(tBu-Ar); 126.18, 126.44(CH$_2$-Ar); 134.38, 134.59, 135.51, 136.20(H-Ar); 136.86, 137.86, 138.44, 138.82(H-Ar); 162.45, 162.57, 163.53, 164.01(O-Ar); 211.14, 216.81 (carbene C). Anal. Calcd for $C_{72}H_{108}N_4O_5YK$: C, 70.07; H, 8.65; N, 4.81.

Found: C, 69.90; H, 8.82; N, 4.48.

Synthesis of L1$_3$Sm$_2$Cl$_3$(3). In a THF solution, **L1** (0.20g, 0.37mmol) was reacted with Sm[N(SiMe$_3$)$_2$]$_3$ (0.24mmol) or Sm[N(SiMe$_3$)$_2$]$_3$-μ-Cl-Li(THF)$_3$ (0.24mmol) and stirred overnight at room temperature, and then the solvent was removed under vacuum and extracted by hexane/THF solvent mixture. Colorless block crystals were obtained at room temperature in 1-2 days. Anal. Calcd for C102H153N6Cl13O6Sm2: C, 62.30; H, 7.84; N, 4.27. Found: C, 62.42; H, 7.80; N, 4.24.

Synthesis of L1$_3$Y$_2$Cl$_3$(4). In a THF solution, **L1** (0.20g, 0.37mmol) was reacted with Y[N(SiMe$_3$)$_2$]$_3$ (0.24mmol) and stirred overnight at room temperature, and then the solvent was removed under vacuum and extracted by hexane/THF solvent mixture. Colorless crystals were obtained at room temperature in 1-2 days. ^{1}H NMR (600M, THF-*d*$_8$) δ 0.97(54H, s ,tBu); 1.27(54H, s ,tBu); 1.76(6H, m, NCH$_2$C*H*$_2$CH$_2$N); 3.60, 3.23(12H, m, NC*H*$_2$CH$_2$C*H*$_2$N); 3.57, 3.59(6H, s, NCH$_2$-Ar); 6.47, 6.50(6H, s, NCH$_2$-Ar); 6.95(6H, b, Ar-H); 7.03(6H, b, Ar-H); 9.63(3H, s, C2-H(ring)); ^{13}C NMR (600M, THF-*d*$_8$) δ 20.10(NCH$_2$*C*H$_2$CH$_2$N); 30.60(-C(*C*H$_3$)$_3$); 32.34(-C(*C*H$_3$)$_3$); 34.41(-*C*(CH$_3$)$_3$); 35.71(-*C*(CH$_3$)$_3$); 42.91(N*C*H$_2$CH$_2$*C*H$_2$N); 56.62(N*C*H$_2$-Ar); 123.96(tBu-Ar); 123.98(tBu-Ar); 125.70(CH$_2$-Ar); 135.59(H-Ar); 138.89(H-Ar); 153.41(N*C*HN); 162.29, 162.32(O-Ar). Anal. Calcd for C102H153N6Cl13O6Y2: C, 66.46; H, 8.37; N, 4.56. Found: C, 67.09; H, 8.45; N, 4.40.

Typical Procedure for the polymerization of *n*-hexyl isocyanate. All the polymerizations were carried out in purified argon atmosphere using Schlenk technique and the polymerizations procedure catalyzed by complexes **1-2**, **5-7** were similar. In a dry and oxygen-free 20ml flask, *n*-hexyl isocyanate (about 0.4g) and desired toluene was added. The flask was placed in a -20°C atmosphere, and then desired amount of complex **1** was added and the system became viscous very quickly. The reaction was quenched by adding excess methanol after the prescribed time. The polymer was precipitated and dried under vacuum and weighed.

X-ray Crystallographic Study. Single crystals of complexes **1** and **3** were sealed in liquid paraffin oil for determination of the single-crystal structures. Data were collected at 170K on a CrysAlisPro, Oxford Diffraction Ltd. using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All structures were solved by direct methods, and refined by full-matrix least-square methods based on $|F|^2$. The structures were solved and refined using SHELX-97 programs. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. Crystal and refinement data for complexes **1** and **3** are given in Table s1.

Acknowledgements

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (21174121), the Special Funds for Major Basic Research Projects (G2011CB606001), and Zhejiang Provincial Natural Science Foundation of China (LY13B040001). We thank Dr. Jun Ling and Mr. Fangyu Hu (Zhejiang University) for helpful discussions.

Notes and references

1. (a) S. Bellemin-Laponnaz and S. Dagorne, *Chem. Rev.*, 2014, **114**, 8747-8774; (b) L. Palacios, A. Di Giuseppe, A. Opalinska, R. Castarlenas, J. J. Pérez-Torrente, F. J. Lahoz and L. A. Oro, *Organometallics*, 2013, **32**, 2768-2774; (c) P. Horeglad, O. Ablialimov, G. Szczepaniak, A. M. Dąbrowska, M. Dranka and J. Zachara, *Organometallics*, 2014, **33**, 100-111; (d) D. Zhang and G. Zi, *Chem. Soc. Rev.*, 2015, **44**, 1898-1921; (e) G. J. Barbante, E. H. Doeven, P. S. Francis, B. D. Stringer, C. F. Hogan, P. R. Kheradmand, D. J. D. Wilson and P. J. Barnard, *Dalton Trans.*, 2015, **44**, 8564-8576; (f) P. L. Arnold, I. J. Casely, Z. R. Turner, R. Bellabarba and R. B. Tooze, *Dalton Trans.*, 2009, **35**, 7236-7247; (g) S. T. Liddle, I. S. Edworthy and P. L. Arnold, *Chem. Soc. Rev.*, 2007, **36**, 1732-1744; (h) P. L. Arnold and S. T. Liddle, *Chem. Commun.*, 2006, **38**, 3959-3971; (i) D. Zhang, S. Zhou, Z. Li, Q. Wang and L. Weng, *Dalton Trans.*, 2013, **42**, 12020-12030; (j) Z. Wang, L. Jiang, D. K. B. Mohamed, J. Zhao and T. S. A. Hor, *Coord. Chem. Rev.*, 2015, **293–294**, 292-326.
2. (a) C. Romain, S. Choua, J. P. Collin, M. Heinrich, C. Bailly, L. Karmazin-Brel1t, S. Bellemin-Laponnaz and S. Dagorne, *Inorg. Chem.*, 2014, **53**, 7371-7376; (b) D. Zhang and H. Kawaguchi, *Organometallics*, 2006, **25**, 5506-5509; (c) D. Zhang and N. Liu, *Organometallics*, 2009, **28**, 499-505; (d) Y. Kong, H. Ren, S. Xu, H. Song, B. Liu and B. Wang, *Organometallics*, 2009, **28**, 5934-5940; (e) D. R. Weinberg, N. Hazari, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2010, **29**, 89-100; (f) C. Romain, L. Brelot, S. Bellemin-Laponnaz and S. Dagorne, *Organometallics*, 2010, **29**, 1191-1198; (g) Y. Kong, M. Cheng, H. Ren, S. Xu, H. Song, M. Yang, B. Liu and B. Wang, *Organometallics*, 2011, **30**, 1677-1681; (h) S. Dagorne, S. Bellemin-Laponnaz and C. Romain, *Organometallics*, 2013, **32**, 2736-2743; (i) E. Despagnet-Ayoub, L. M. Henling, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2013, **32**, 2934-2938; (j) E. Borré, G. Dahm, A. Aliprandi, M. Mauro, S. Dagorne and S. Bellemin-Laponnaz, *Organometallics*, 2014, **33**, 4374-4384; (k) C. Romain, C. Fliedel, S. Bellemin-Laponnaz and S. Dagorne, *Organometallics*, 2014, **33**, 5730-5739; (l) L. Dang, H. Song and B. Wang, *Organometallics*, 2014, **33**, 6812-6818; (m) E. Despagnet-Ayoub, K. Miqueu, J. M. Sotiropoulos, L. M. Henling, M. W. Day, J. A. Labinger and J. E. Bercaw, *Chem. Sci.*, 2013, **4**, 2117-2121; (n) H. Aihara, T. Matsuo and H. Kawaguchi, *Chem. Commun.*, 2003, **17**, 2204-2205; (o) S. Bellemin-Laponnaz, R. Welter, L. Brelot and S. Dagorne, *J. Organomet. Chem.*, 2009, **694**, 604-606; (p) S. Barroso, S. R. M. M. de Aguiar, R. F. Munhá and A. M. Martins, *J. Organomet. Chem.*, 2014, **760**, 60-66; (q) M. Nirmala, G. Prakash, P. Viswanathamurthi and J. G. Malecki, *J. Mol. Catal. A: Chem.*, 2015, **403**, 15-26; (r) A. El-Batta, A. W. Waltman and R. H. Grubbs, *J. Organomet. Chem.*, 2011, **696**, 2477-2481.
3. D. Zhang, H. Aihara, T. Watanabe, T. Matsuo and H. Kawaguchi, *J. Organomet. Chem.*, 2007, **692**, 234-242.
4. D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39-92.
5. (a) C. Yao, C. Wu, B. Wang and D. Cui, *Organometallics*, 2013, **32**, 2204-2209; (b) K. Lv and D. Cui, *Organometallics*, 2008, **27**, 5438-5440; (c) Z. Wang, H. Sun, H. Yao, Y. Yao, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2006, **691**, 3383-3390; (d) P. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, R. Bellabarba and R. P. Tooze, *Dalton Trans.*, 2010, **39**, 6808-6814; (e) L. Maron and D. Bourissou, *Organometallics*, 2007, **26**, 1100-1103; (f) Z. Li, M. Xue, H. Yao, H. Sun, Y. Zhang and Q.

Shen, *J. Organomet. Chem.*, 2012, **713**, 27-34; (g) J. Zhang, H. Yao, Y. Zhang, H. Sun and Q. Shen, *Organometallics*, 2008, **27**, 2672-2675; (h) P. L. Arnold and S. T. Liddle, *Chem. Commun.*, 2006, **38**, 3959-3971; (i) P. L. Arnold, S. A. Mungur, A. J. Blake and C. Wilson, *Angew. Chem.,* 2003, **115**, 6163-6166; (j) M. Zhang, X. Ni and Z. Shen, *Organometallics*, 2014, **33**, 6861-6867; (k) W. Xie, H. Hu and C. Cui, *Angew. Chem.,* 2012, **124**, 11303-11306; (l) W. Xie, H. Hu and C. Cui, *Angew. Chem., Int. Ed.*, 2012, **51**, 11141-11144; (m) Y. Hu, G. M. Miyake, B. Wang, D. Cui and E. Y. X. Chen, *Chem. Eur. J.*, 2012, **18**, 3345-3354; (n) H. Yao, Y. Zhang, H. Sun and Q. Shen, *Eur. J. Inorg. Chem.*, 2009, **13**, 1920-1925; (o) C. Yao, F. Lin, M. Wang, D. Liu, B. Liu, N. Liu, Z. Wang, S. Long, C. Wu and D. Cui, *Macromolecules*, 2015, **48**, 1999-2005; (p) P. L. Arnold and S. T. Liddle, *Organometallics*, 2006, **25**, 1485-1491; (q) B. Wang, D. Wang, D. Cui, W. Gao, T. Tang, X. Chen and X. Jing, *Organometallics*, 2007, **26**, 3167-3172; (r) H. Yao, J. Zhang, Y. Zhang, H. Sun and Q. Shen, *Organometallics*, 2010, **29**, 5841-5846; (s) X. Gu, X. Zhu, Y. Wei, S. Wang, S. Zhou, G. Zhang and X. Mu, *Organometallics*, 2014, **33**, 2372-2379; (t) P. L. Arnold, J. McMaster and S. T. Liddle, *Chem. Commun.*, 2009, **7**, 818-820; (u) D. Patel, S. T. Liddle, S. A. Mungur, M. Rodden, A. J. Blake and P. L. Arnold, *Chem. Commun.*, 2006, **10**, 1124-1126; (v) B. Wang, T. Tang, Y. Li and D. Cui, *Dalton Trans.*, 2009, **41**, 8963-8969; (w) T. Mehdoui, J.-C. Berthet, P. Thuery and M. Ephritikhine, *Chem. Commun.*, 2005, **22**, 2860-2862; (x) P. L. Arnold, T. Cadenbach, I. H. Marr, A. A. Fyfe, N. L. Bell, R. Bellabarba, R. P. Tooze and J. B. Love, *Dalton Trans.*, 2014, **43**, 14346-14358; (y) W. Fegler, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2010, **39**, 6774-6779; (z) P. L. Arnold, Z. R. Turner, A. I. Germeroth, I. J. Casely, G. S. Nichol, R. Bellabarba and R. P. Tooze, *Dalton Trans.*, 2013, **42**, 1333-1337； (aa) P. L. Arnold, I. A. Marr, S. Zlatogorsky, R. Bellabarba and R. P. Tooze, *Dalton Trans.*, 2014, **43**, 34-37; (ab) W. Fegler, T. Saito, K. Mashima, T. P. Spaniol and J. Okuda, *J. Organomet. Chem.*, **695**, 2794-2797; (ac) Y. Pan, T. Xu, Y.-S. Ge and X.-B. Lu, *Organometallics*, 2011, **30**, 5687-5694.

6. (a) M. Zhang, Z. Liang, J. Ling, X. Ni and Z. Shen, *Dalton Trans.*, 2015, **44**, 11182-11190; (b) Z. Liang, X. Ni, X. Li and Z. Shen, *Dalton Trans.*, 2012, **41**, 2812-2819; (c) K. Nie, X. Gu, Y. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2010, **39**, 6832-6840; (d) F. Bonnet, H. E. Dyer, Y. El Kinani, C. Dietz, P. Roussel, M. Bria, M. Visseaux, P. Zinck and P. Mountford, *Dalton Trans.*, 2015, 44, 12312-12325; (e) F. Bonnet, A. R. Cowley and P. Mountford, *Inorg. Chem.*, 2005, **44**, 9046-9055.; (f) Y. Yao, M. Ma, X. Xu, Y. Zhang, Q. Shen and W. Wong, *Organometallics*, 2005, **24**, 4014-4020; (g) T. Zeng, Q. Qian, Y. Wang, Y. Yao and Q. Shen, *J. Organomet. Chem.*, 2015, **779**, 14-20; (h) T. Zeng, Y. Wang, Q. Shen, Y. Yao, Y. Luo and D. Cui, *Organometallics*, 2014, **33**, 6803-6811; (i) T. Zeng, Q. Qian, B. Zhao, D. Yuan, Y. Yao and Q. Shen, *RSC Adv.*, 2015, **5**, 53161-53171; (j) J. Ling and Z. Shen, *Macromol. Chem. Phys.*, 2002, **203**, 735-738; (k) Z. Liang, X. Ni, X. Li and Z. Shen, *Inorg. Chem. Commun.*, 2011, **14**, 1948-1951; (l) L. Wang, Z. Liang, X. Ni and Z. Shen, *Chin. Chem. Lett.,* 2011, **22**, 249-252; (m) X. Ni, Z. Liang, J. Ling, X. Li and Z. Shen, *Polym. Int.*, 2011, **60**, 1745-1752; (n) J. Ling, W. Zhu and Z. Shen, *Macromolecules*, 2004, **37**, 758-763.
7. (a) N. Fukuwatari, H. Sugimoto and S. Inoue, *Macromol. Rapid Comm.*, 1996, **17**, 1-7; (b) A. Touris, K. Kostakis, S. Mourmouris, V. Kotzabasakis, M. Pitsikalis and N. Hadjichristidis, *Macromolecules*, 2008, **41**, 2426-2438; (c) X. Liu, J. Deng, Y. Wu and L. Zhang, *Polymer*, 2012, **53**, 5717-5722; (d) T. E. Patten and B. M. Novak, *J. Am. Chem. Soc.*, 1991, **113**, 5065-5066; (e) A. J. Bur and L. J. Fetters, *Chem. Rev.*, 1976, **76**, 727-746.
8. (a) V. E. Shashoua, W. Sweeny and R. F. Tietz, *J. Am. Chem. Soc.*, 1960, **82**, 866-873; (b) V. E. Shashoua, *J. Am. Chem. Soc.*, 1959, **81**, 3156-3156.
9. (a) Y. D. Shin, S. Y. Kim, J. H. Ahn and J. S. Lee, *Macromolecules*, 2001, **34**, 2408-2410; (b) J. S. Lee and S. W. Ryu, *Macromolecules*, 1999, **32**, 2085-2087; (c) A. Vazaios, M. Pitsikalis and N. Hadjichristidis, *J. Polym. Sci. Polym. Chem.*, 2003, **41**, 3094-3102.
10. J. Min, P. N. Shah, J. H. Ahn and J. S. Lee, *Macromolecules*, 2011, **44**, 3211-3216.
11. T. E. Patten and B. M. Novak, *Makromol. Chem. Macromol. Symp.*, 1993, **67**, 203-211.
12. K. Tanaka, M. Furo, E. Ihara and H. Yasuda, *J. Polym. Sci. Polym. Chem.*, 2001, **39**, 1382-1390.
13. (a) X. Yang, X. Ni and Z. Shen, *Sci. China Ser. B-Chem.*, 2009, **52**, 1843-1850; (b) J. Jiao, X. Yang and X. Ni, *Acta Polym Sin*, 2011, **5**, 475–480; (c) X. Ni, X. Xu and Z. Shen, *J Appl. Polym. Sci.*, 2007, **103**, 2135-2140; (d) X. Xu, X. Ni and Z. Shen, *Polym. Bull.*, 2005, **53**, 81-88; (e) E. Ihara, Y. Adachi, H. Yasuda, H. Hashimoto, N. Kanehisa and Y. Kai, *J. Organomet. Chem.*, 1998, **569**, 147-157; (f) H. Wang, H. Li, X. Yu, Z. Ren and J. Lang, *Tetrahedron*, 2011, **67**, 1530-1535; (g) H. Yasuda, *J. Organomet. Chem.*, 2002, **647**, 128-138; (h) T. Ikeda, H. Sugimoto and S. Inoue, *J. Macromol. Sci. A*, 1997, **34**, 1907-1920.
14. V. T. Kasumov and F. Köksal, *Spectrochim. Acta A,* 2005, **61**, 225-231.
15. P. L. Arnold and I. J. Casely, *Chem. Rev.*, 2009, **109**, 3599-3611.
16. P. Liu, M. Wesolek, A. A. Danopoulos and P. Braunstein, *Organometallics*, 2013, **32**, 6286-6297.
17. (a) A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J. F. Carpentier, *Angew. Chem.,* 2006, **118**, 2848-2850; (b) N. Ajellal, D. M. Lyubov, M. A. Sinenkov, G. K. Fukin, A. V. Cherkasov, C. M. Thomas, J. F. Carpentier and A. A. Trifonov, *Chem. Eur. J.*, 2008, **14**, 5440-5448.
18. X. Xu, X. Ni, X. Hong and Z. Shen, *Chem. Res. Chinese U.*, 2005, **21**, 224-226.
19. S. Mourmouris, K. Kostakis, M. Pitsikalis and N. Hadjichristidis, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 6503-6514.
20. S. Zhou, S. Wang, G. Yang, X. Liu, E. Sheng, K. Zhang, L. Cheng and Z. Huang, *Polyhedron*, 2003, **22**, 1019-1024.
21. (a) F. T. Edelmann, A. Steiner, D. Stalke, J. W. Gilje, S. Jagner and M. H»kansson, *Polyhedron*, 1994, **13**, 539-546; (b) D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, **10**, 1021-1023.

Polyhexyl isocyananates catalyzed by N-heterocyclic carbene rare earth metal complexes show high molecular weight with narrow molecular weight distribution.