Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

Cite this: *Dalton Trans.*, 2014, **43**, 2244

Living ring-opening homo- and copolymerisation of ε-caprolactone and L-lactide by cyclic β-ketiminato aluminium complexes†

Yan Liu,[a,b] Wei-Shi Dong,[a] Jing-Yu Liu*[a] and Yue-Sheng Li[a]

A series of novel aluminium complexes containing cyclic β-ketiminato ligands of type $Me_2Al\{O-[(ArN{=}CHC_4H_4(C_6H_4))]\}$ (**3a**, Ar = 2,6-$^iPr_2C_6H_3$; **3b**, Ar = C_6H_5; **3c**, Ar = C_6F_5) have been prepared in high yields. These complexes were identified by ^1H, ^{13}C NMR spectroscopy and elemental analysis. X-ray structural analyses for **3a–c** revealed that these complexes have a distorted tetrahedral geometry around Al, and both bond distances and bond angles were considerably influenced by the ligand structure. These complexes were tested as catalyst precursors for ring-opening polymerisation of ε-caprolactone (ε-CL) and L-lactide (L-LA) in the presence of 2-propanol as an initiator. Complex **3a** could polymerize ε-CL in a controlled manner with high efficiency. Based on the living characteristics, the preparation of well-defined block copolymers PCL-*b*-PLLA *via* sequential addition of monomers was performed by **3a**. Note that complex **3c** exhibited rather high catalytic activity for the ROP of L-LA with narrow molecular weight distribution. The monomer conversion reached completion only in 4 h when the L-LA/Al molar ratio was 100 at 80 °C. PLLA-*b*-PCL copolymers were thus easily produced by **3c**.

Received 30th September 2013,
Accepted 22nd October 2013

DOI: 10.1039/c3dt52712c

www.rsc.org/dalton

Introduction

The ring-opening polymerisation (ROP) of cyclic esters, such as ε-caprolactone (ε-CL) and lactide (LA), promoted by metal catalysts *via* a coordination–insertion mechanism is an effective method for the synthesis of biodegradable and biocompatible materials due to the advantages of well controlled molecular weights and low polydispersity indices.[1–4] The physical properties and functional parameters of poly(ε-caprolactone) (PCL) are quite different from those of polylactide (PLA). For instance, PCL has notable drug permeability, elasticity and thermal properties, while PLA exhibits excellent mechanical properties but poor elasticity.[5] The ε-CL/LA copolymerisation thus allowed the properties of the resultant polyesters to be tuned by changing the composition and the distribution of the monomer repeat units along the copolymer chain.[6–20] A variety of complexes of aluminium, tin, and transition metals have been used to synthesize ε-CL/LA block copolymers.[12–20] Note that the order of monomer addition was very important to obtain well-defined block polymers. When the ε-CL monomer was polymerized first, the living PCL* macromolecules were then able to initiate LA polymerisation and give rise to diblock copolymer PCL-*b*-PLA effectively. However, reports of the living PLA* initiating ε-CL polymerisation in a living manner are limited so far.

Aluminium alkoxide-based initiator systems seem to be active and suited for the ROP of cyclic esters on account of their high Lewis acidity and low toxicity. Many four coordination aluminium complexes have proven to initiate the living ROP of ε-caprolactone, producing polymers with well-controlled molecular weights and narrow molecular weight distributions.[21–30] Nevertheless, almost all low coordinated Schiff-base aluminium catalysts only exhibit relatively low efficiency in L-LA polymerisation.[31–37] Our aim is to obtain highly efficient aluminium catalysts not only for ε-CL polymerisation but also for L-LA polymerisation, to prepare well-defined block polymers (PCL-*b*-PLA and PLA-*b*-PCL). Recently, we have reported a new class of neutral nickel complexes based on cyclic β-ketiminato ligands, which displayed highly active for ethylene polymerisation without an activator. As part of our investigation of β-ketiminato ligands in homogeneous polymerisation catalysis, we were interested in preparing a new family of aluminium complexes containing cyclic β-ketiminato ligands. Herein, we thus described the synthesis and characterization of some novel four coordination aluminium

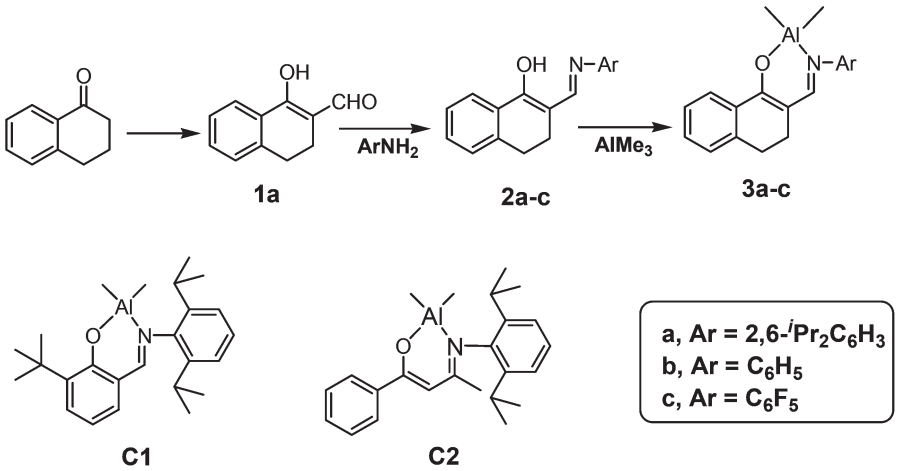
[a]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: ljy@ciac.jl.cn*

[b]*College of Environment & Chemical Engineering, Yanshan University, Qinhuangdao 066004, China*

†Electronic supplementary information (ESI) available: Crystal data and structure refinements of complexes **3a–c**; the structures for **3b–c** and X-ray diffraction data for **3a–c** as cif; ^{13}C NMR spectra of PCL-*b*-PLLA and PLLA-*b*-PCL; DSC curve of PCL-*b*-PLLA; GPC curves of PLLA and PLLA-*b*-PCL. CCDC 946613–946615. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52712c

This journal is © The Royal Society of Chemistry 2014

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.



Scheme 1

complexes containing cyclic β-ketiminato ligands of type $Me_2Al\{O\text{-}[(ArN{=}CHC_4H_4(C_6H_4))]\}$ (**3a**, Ar = 2,6-$^{i}Pr_2C_6H_3$; **3b**, Ar = C_6H_5; **3c**, Ar = C_6F_5) (Scheme 1), and explored their application for the ROP of ε-CL and L-LA. Activated by 2-propanol as an initiator, these complexes proved to be highly active towards the polymerisation of ε-CL and L-LA, allowing a well-controlled chain growth. We also explored CL/LA copolymerisation with these complexes to prepare block copolymers.

Results and discussion

Synthesis of aluminium complexes

A series of novel aluminium complexes containing cyclic β-ketiminato ligands of the type, $Me_2Al\{O\text{-}[(ArN{=}CHC_4H_4(C_6H_4))]\}$ (**3a**, Ar = 2,6-$^{i}Pr_2C_6H_3$; **3b**, Ar = C_6H_5; **3c**, Ar = C_6F_5), were effectively prepared *via* the reaction of $AlMe_3$ with 1.0 equiv. of the corresponding neutral ligand $[ArN{=}CHC_4H_4(C_6H_4)]OH$ in toluene, as shown in Scheme 1. These reactions took place along with the evolution of methane, and the analytically pure samples were collected from the chilled concentrated mixture of toluene and *n*-hexane solution containing Al complexes cooled in the freezer (−20 °C). The resultant complexes were identified by ^{1}H and ^{13}C NMR spectra and elemental analysis. The formulations of alkyl aluminium complexes **3a–c** are consistent with the NMR spectroscopic data and elemental analyses. A sharp single resonance assigned to the Al-*Me* protons and the resonances corresponding to the ligands were observed. Crystals of **3a–c** suitable for X-ray crystal analysis were grown from the chilled concentrated CH_2Cl_2 and *n*-hexane mixture solution. The crystallographic data together with the collection and refinement parameters are summarized in Table S1,† and the selected bond distances and angles are summarized in Table 1.

The structure of **3a** is shown in Fig. 1. Complex **3a** adopted a distorted tetrahedral geometry around the Al metal centre, as seen in the bond angles for C(1)–Al–C(2) (115.23(10)°), O(1)–

Table 1 Selected bond distances (Å) and angles (°) for complexes **3a–c**

	3a	**3b (A)**	**3b (B)**	**3c**
		Bond distances in Å		
Al(1)–O(1)	1.8021(13)	1.8028(17)	1.7943(17)	1.8121(18)
Al(1)–N(1)	1.9366(15)	1.948(2)	1.946(2)	1.974(2)
Al(1)–C(1)	1.958(2)	1.957(3)	1.957(3)	1.950(3)
Al(1)–C(2)	1.960(2)	1.954(3)	1.955(3)	1.945(3)
N(1)–C(4)	1.454(2)	1.436(3)	1.439(3)	1.414(3)
O(1)–C(11)	1.310(2)	1.307(3)	1.310(3)	1.304(3)
		Bond angles in °		
O(1)–Al(1)–N(1)	93.44(6)	93.85(8)	94.26(8)	92.47(8)
C(1)–Al(1)–C(2)	115.23(10)	118.15(12)	116.93(12)	120.86(12)
Al(1)–O(1)–C(11)	128.77(12)	129.32(16)	130.45(16)	123.48(16)
Al(1)–N(1)–C(3)	121.07(12)	122.05(16)	122.32(16)	117.10(16)
Al(1)–N(1)–C(4)	123.42(11)	120.16(15)	119.48(16)	125.03(16)
O(1)–Al(1)–C(1)	113.88(8)	110.87(11)	112.59(10)	110.01(10)
O(1)–Al(1)–C(2)	109.45(8)	110.76(10)	109.16(10)	105.34(11)
N(1)–Al(1)–C(1)	109.39(8)	109.74(11)	107.24(10)	113.87(10)
N(1)–Al(1)–C(2)	113.52(8)	110.82(11)	114.47(11)	110.17(11)

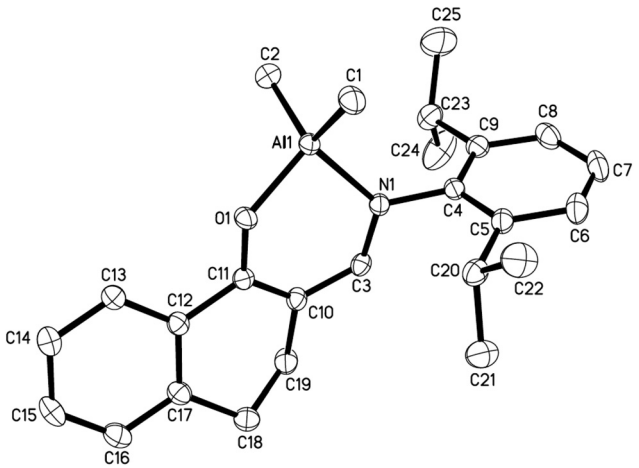


Fig. 1 Molecular structure of complex **3a** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

Table 2 Ring-opening polymerisation of ε-caprolactone and L-lactide by the **3a–c**/^{i}PrOH system[a]

Entry	Complex	Time	Monomer	Conversion (%)	$M_{n,calcd}$ [b,c] (10^{-4})	M_n [d] (10^{-4})	M_w/M_n
1	**3a**	20 s	ε-CL	27	0.31	0.39	1.06
2	**3a**	1 min	ε-CL	63	0.72	0.87	1.07
3	**3a**	3 min	ε-CL	92	1.05	1.22	1.09
4	**3a**	5 min	ε-CL	>99	1.15	1.31	1.10
5	**3b**	10 min	ε-CL	86	0.99	0.95	1.15
6	**3c**	10 min	ε-CL	94	1.08	1.28	1.17
7	**3a**	4 h	L-LA	58	0.84	0.65	1.05
8	**3b**	4 h	L-LA	71	1.03	0.85	1.05
9	**3c**	0.5 h	L-LA	35	0.51	0.39	1.05
10	**3c**	1 h	L-LA	64	0.93	0.72	1.06
11	**3c**	2 h	L-LA	88	1.27	1.00	1.07
12	**3c**	3 h	L-LA	96	1.39	1.12	1.08
13	**3c**	4 h	L-LA	>99	1.45	1.20	1.12
14	**C1**	4 h	L-LA	Trace	—	—	—
15	**C2**	4 h	L-LA	17	0.25	0.28	1.08

[a] Reaction conditions: 20–50 μmol Al catalyst in toluene, ^{i}PrOH 1.0 equiv. to Al, monomer 5.0 mmol, monomer/Al (molar ratio) = 100, 80 °C. [b] Calculated by $([CL]_0/[OH]_0) \times 114.14 \times$ conv. (%) + ^{i}PrOH. [c] Calculated by $([LA]_0/[OH]_0) \times 144.13 \times$ conv. (%) + ^{i}PrOH. [d] GPC data in THF *vs.* polystyrene standards, using a correcting factor 0.56 for PCL and 0.58 for PLA.

Al–C(1) (113.88(8)°), and O(1)–Al–C(2) (109.45(8)°), although the O(1)–Al–N(1) bond angle was somewhat small (93.44(6)°). These bond angles are somewhat analogous to those in Me_2Al-[O-2-^{t}Bu$_2$-6-{(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH}C$_6$H$_3$] (**C1**).[22,23] The Al–O(1) bond length is 1.8021(13) Å, indicating O atom formed a σ-bond with Al. The Al–N(1) bond distance is 1.9366(15) Å in complex **3a**, indicative of significant coordination of nitrogen atom to the metal center. In the solid state, the six-membered Al–N–C–C–C–O ring is nearly planar. The structures of **3b** and **3c**, determined by X-ray crystallography are shown in Fig. S1 and S2,† with selected bond distances and angles summarized in Table 1. Crystals of **3b** consist of two crystallographically independent molecules in the unit cell, with only minor differences from each other. These complexes have a distorted tetrahedral geometry around Al. The Al–N bond distances in a series of **3a–c** increased in the order: **3a** (1.9366(15) Å) < **3b** (1.948(2), 1.946(2) Å) < **3c** (1.974(2) Å). The C(1)–Al–C(2) bond angles increased in the order: **3a** (115.23(10)°) < **3b** (118.15(12), 116.93(12)°) < **3c** (120.86(12)°). These results indicated that the bond distances and angles in Me_2Al{O–[(ArN=CHC$_4$H$_4$(C$_6$H$_4$))]} are influenced by the substituents in the imino groups.

Homopolymerisation of ε-caprolactone and L-lactide

Homopolymerisation of ε-CL and L-LA were explored in the presence of ^{i}PrOH (1.0 equiv. to Al), and typical results are summarized in Table 2. At a monomer/metal molar ratio of 100, the **3a**/^{i}PrOH system displayed rather high activity for the ROP of ε-CL, the monomer conversion nearly reached completion after 5 min (entries 1–4). A linear relationship was observed between the monomer conversions and the number of average molecular weight (M_n) values with narrow molecular weight distributions (MWDs) (Fig. 2). Moreover, the polymerisation rate of the ROP was first-order dependent on the monomer concentration (Fig. 3), suggesting no deactivation of active species during the ROP of ε-CL. It was therefore clear

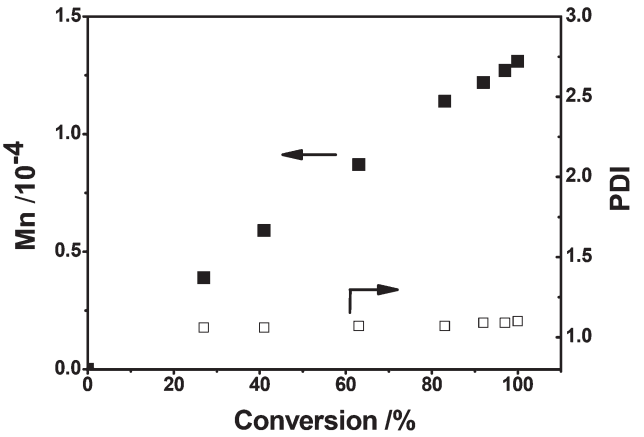


Fig. 2 M_n (■) and M_w/M_n (□) *vs.* monomer conversion in the ROP of ε-CL initiated by the **3a**/^{i}PrOH system.

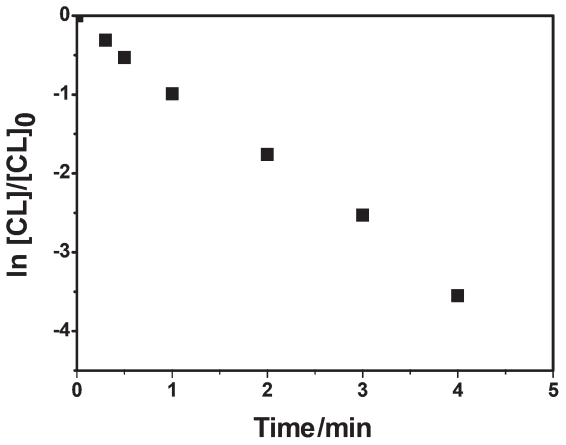


Fig. 3 Time course plots of Ln[CL]/[CL]$_0$ ([CL] = concentration of CL in mmol mL^{-1}).

 This journal is © The Royal Society of Chemistry 2014

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

that the ROP by the **3a**/^{i}PrOH system proceeded in a living manner under these conditions.

The ROP of ε-CL catalyzed by **3b**, without any substituent, took place less efficiently than that by catalyst **3a** (entry 5), and the monomer conversion only reached 86% in 10 min. Complex **3c** with a fluorinated ligand exhibited improved catalytic performance for the ROP of ε-CL compared with **3b**, affording PCLs with narrow MWD (entry 6). Taking these results into account, it is therefore clear that the catalyst structure significantly influenced the polymerisation behaviors. The signals assigned to the hydroxy end group (–CH_2OH) and the isopropyl ester end-group ((CH_3)$_2$CHO(CO)) were observed in ^{1}H NMR spectra of polylactones prepared by **3a**, indicating that the polymerisation involved the selective rupture of the acyl–oxygen bond of the monomer and the insertion into the alkoxide–aluminium bond.

The ROP of L-lactide initiated by complexes **3a–c** was also investigated, as shown in Table 2. The catalytic activity in the ROP of L-LA with a series of $Me_2Al\{O\text{-}[(ArN{=}CHC_4H_4(C_6H_4))]\}$ increased in the order: **3a** < **3b** < **3c**. Complex **3a** showed the lowest activity for L-LA polymerisation among these catalysts under similar conditions. The observed result was an interesting contrast to that found for ε-CL polymerisation, in which **3a** exhibited highest catalytic activities. It should be noted that using analogue **3c** brought about obvious improvements in the catalytic performances for ROP of L-LA. The monomer conversion nearly reached completion only in 4 h (entry 13). The M_n values linearly increased for longer reaction time with consistently low PDI values (Fig. 4). The same first-order relationship between the M_n values and the yields was observed under these conditions (Fig. 5). These results indicated that the catalyst **3c** could polymerize L-LA in a controlled manner. The resulting PLA macromolecular chain is capped with the hydroxyl group at one end, and with the ^{i}PrO- group at the other end, suggesting probably a coordination insertion mechanism.

The salicylaldiminato aluminium analogue $Me_2Al[O\text{-}2\text{-}^{t}Bu\text{-}6\text{-}\{(2,6\text{-}^{i}Pr_2C_6H_3)N{=}CH\}C_6H_3]$ (**C1**) and β-enaminoketonato aluminium complex (**C2**) were prepared for comparison. The results are also listed in Table 3. Neither **C1**/^{i}PrOH nor **C2**/^{i}PrOH was an efficient catalyst system for the ROP of L-LA, only a tiny amount of polymer was obtained after 4 h at 80 °C (entries 14 and 15). These results provided further evidence of the advantage of using these novel four coordination aluminium complexes bearing a cyclic β-ketiminato ligand in the ROP of cyclic esters.

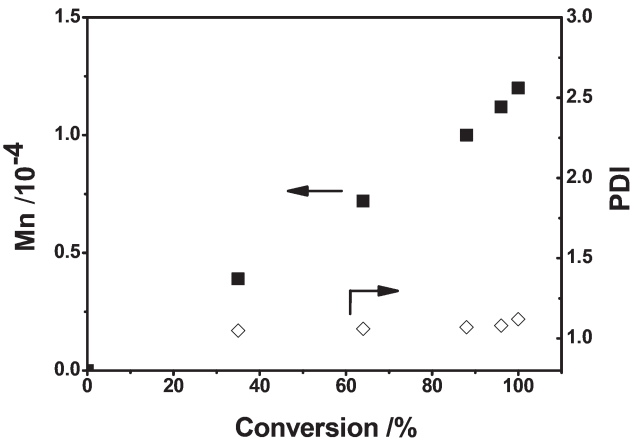


Fig. 4 M_n (■) and M_w/M_n (□) *vs.* monomer conversion in the ROP of L-LA initiated by the **3c**/^{i}PrOH system.

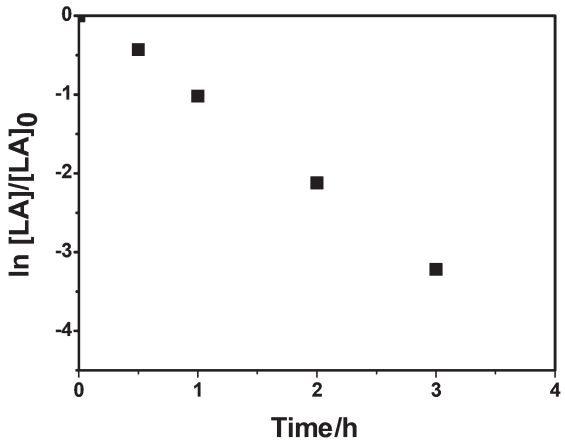


Fig. 5 Time course plots of Ln[LA]/[LA]$_0$ ([LA] = concentration of LA in mmol mL^{-1}).

Copolymerisation of ε-caprolactone and L-lactide

The living characters of both ε-CL and L-LA homopolymerisation catalyzed by new aluminium complexes allowed the preparation of well-defined block copolymers *via* sequential addition of the two monomers.

Synthesis of PCL-*b*-PLLA diblock copolymers

The L-LA monomer was added after the first step polymerisation of ε-CL had gone to completion. A typical result is summarized in Table 3. As expected, the M_n value of the copolymer increased with the growth of the chain segment, and the MWD of the copolymer only changed slightly. For example, the M_n increased from 23 400 (PDI = 1.10) for the first chain segment to 33 400 (PDI = 1.17) for the second chain segment with a unimodal peak (Fig. 6).

In the ^{1}H NMR spectrum (Fig. 7), the signals due to methylene protons of the hydroxyl end groups (–*CH_2*–OH) of the PCL at 3.65 ppm completely disappeared and a new signal corresponding to –*CH*(CH_3)OH, methyne proton of the hydroxyl end group of the copolymer appeared at 4.25 ppm, indicating that the PCL reactive chain end initiated the polymerisation of L-LA. Besides, the ^{13}C NMR spectra of the copolymers exhibited two carbonyl resonances at 173.3 and 169.4 ppm corresponding to the PCL and PLA blocks (Fig. S3†). The thermal analysis of the copolymers by DSC shows two melting peaks (T_m) corresponding to PCL and PLLA blocks, respectively (Fig. S4†). Taking these results into account, it is therefore clear that the block copolymer PCL-*b*-PLLA was formed.

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

Table 3 Synthesis of diblock copolymers from cyclic ester monomers[a]

Entry	Complex	Time	Conversion (%)	$M_{n,SEC}$ [b] (10^{-4})	M_n [c,d] (10^{-4})	M_w/M_n [b]
1 PCL-*b*-PLLA[e]	**3a**	5 min (CL) + 4 h (LA)	73	3.34	1.89	1.17
2 PLLA-*b*-PCL[f]	**3c**	4 h (LA) + 1.5 h (CL)	91	3.91	2.23	1.32

[a] Reaction conditions: 50 μmol complex in toluene, ^{i}PrOH 1.0 equiv. to Al, monomer 5.0 mmol, Cl/LA/Al = 100/100/1, 80 °C. [b] GPC data determined by SEC in THF relative to polystyrene standards. [c,d] GPC data determined by SEC in THF relative to polystyrene standards corrected by the Mark–Houwink correction factor ([c] $M_{n,SECcorr} = M_{n,SEC\ raw\ data} \times 0.56 \times \%_{PCL} + M_{n,SEC\ raw\ data} \times 0.58 \times \%_{PLLA}$, [d] $M_{n,SECcorr} = M_{n,SEC\ raw\ data} \times 0.58 \times \%_{PLLA} + M_{n,SEC\ raw\ data} \times 0.56 \times \%_{PCL}$). [e] After reaction with CL for the prescribed time, LA was added and reacted for 4 h. [f] After reaction with LA for 4 h, CL was added and reacted for the prescribed time.

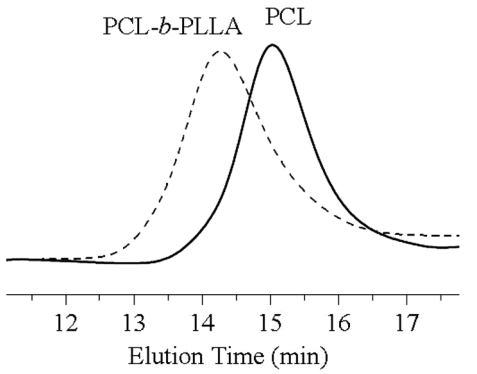


Fig. 6 GPC profiles (in THF at 25 °C) of PCL and PCL-*b*-PLLA obtained by the **3a**/^{i}PrOH system.

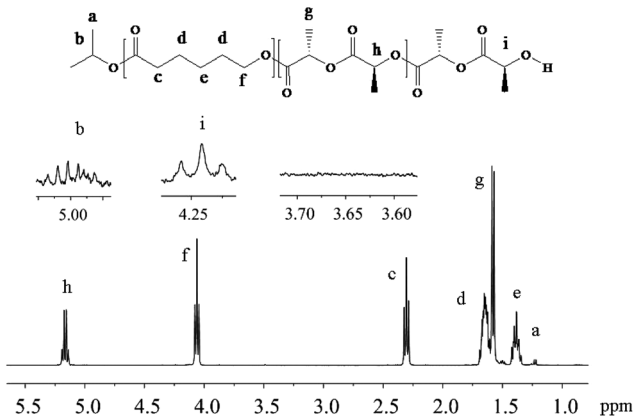


Fig. 7 ^{1}H NMR spectrum of PCL-*b*-PLLA copolymer by catalyst **3a** (entry 1, Table 3).

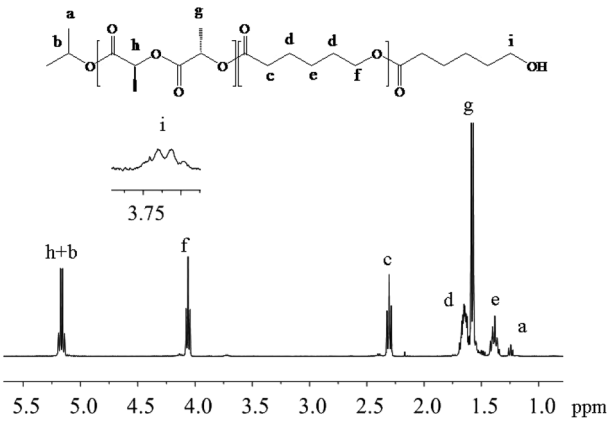


Fig. 8 ^{1}H NMR spectrum of PLLA-*b*-PCL copolymer by catalyst **3c** (entry 2, Table 3).

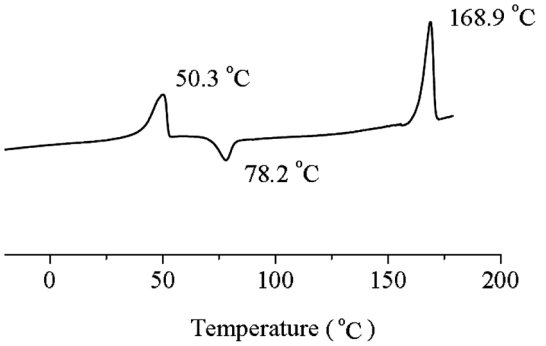


Fig. 9 DSC curve of PLLA-*b*-PCL prepared by catalyst **3c**.

Synthesis of PLLA-*b*-PCL

To further explore the formation of diblock copolymers, the "poly(lactide) block first route" was examined with **3c** by sequential ROP of L-LA and CL in toluene to yield PLLA-*b*-PCL. The result is also summarized in Table 3. SEC plots showed that the block copolymer molar mass was higher than that of the pure PLLA homopolymer (Fig. S5†). The expected signals of the copolymer were observed from ^{1}H NMR (Fig. 8) and ^{13}C NMR spectra (Fig. S6†), similar to those of PCL-*b*-PLLA. The peaks corresponding to the isopropyl ester and hydroxyl methylene chain ends were also seen in the ^{1}H NMR spectrum. The appearance of less intense signals at 2.4 and 4.1 ppm in the ^{1}H NMR spectrum and at 172.8 and 170.9 ppm in the ^{13}C NMR spectrum indicated the occurrence of few transesterification side reactions.

Thermal analysis of the copolymer PLLA-*b*-PCL was carried out by DSC and showed two melting peaks at 50.3 °C (PCL) and 168.9 °C (PLA). Moreover, PLLA-*b*-PCL also crystallized during cooling from the melt (T_c = 78.2 °C), as shown in Fig. 9. A similar observation was also reported in the literature.[38,39] These results indicated that the PLLA chain end was able to initiate PCL chain growth, with reasonably controlled molecular weight distribution.

 This journal is © The Royal Society of Chemistry 2014

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

Conclusions

A series of novel aluminium complexes containing cyclic β-ketiminato ligands of type $Me_2Al\{O\text{-}[(ArN{=}CHC_4H_4(C_6H_4))]\}$ (**3a**, Ar = 2,6-$^{i}Pr_2C_6H_3$; **3b**, Ar = C_6H_5; **3c**, Ar = C_6F_5) have been effectively prepared and characterized. With 2-propanol as an initiator, these well-defined complexes proved to be highly active towards ring-opening polymerisation of L-lactide and ε-caprolactone in a controlled manner. The preparation of well-defined block copolymers PCL-*b*-PLLA *via* sequential addition of two monomers was performed by catalyst **3a**. Note that the aluminium complex bearing a fluorinated ligand possessed excellent catalytic performance for the ROP of L-LA. L-LA polymerisation by **3c** can reach near completion only in 4 h. To the best of our knowledge, this novel complex exhibited the highest catalytic efficiency for the ROP of L-LA among the low coordinated Schiff-base aluminium catalysts reported. Using catalyst **3c**, furthermore, the PLA chain end was able to initiate PCL chain growth, PLLA-*b*-PCL was thus easily produced *via* sequential addition. The present catalyst system is thus a rare example for affording PLA-*b*-PCL with significant catalyst efficiency.

Experimental

General procedures and materials

All manipulations of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from an MBraun SPS system. The NMR data of the ligands and complexes used were obtained using a Bruker 400 MHz spectrometer (400 MHz for ^{1}H, 75.5 MHz for ^{13}C) at ambient temperature, with $CDCl_3$ as the solvent (dried by MS 4 Å). Elemental analyses were recorded on an elemental Vario EL spectrometer. Gel permeation chromatographic (GPC) measurements were carried out using a Waters instrument (515 HPLC pump) equipped with a Wyatt interferometric refractometer, eluted with THF at 25 °C at 1 cm^3 min^{-1}. The molecular weights were calibrated against polystyrene standards. The melting temperatures (T_ms) of the resultant copolymers were measured using a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C min^{-1}, and T_m values were collected after the second heating cycle. Reagent grade $AlMe_3$ in *n*-hexane was purchased from Acros and stored in a bottle in the drybox and was used as received.

Synthesis of aluminium complexes

Synthesis of ligands 2a–c. Various cyclic β-ketiminato ligands $[(ArN{=}CHC_4H_4(C_6H_4))]OH$ (**2a**, Ar = 2,6-$^{i}Pr_2C_6H_3$; **2b**, Ar = C_6H_5; **2c**, Ar = C_6F_5) were prepared according to the literature procedures.[40]

$C_6H_5N{=}CHC_4H_4(C_6H_4)OH$ (2b). Yield: 85%. ^{1}H NMR ($CDCl_3$): δ 11.96 (d, *J* = 11.3 Hz, 1H, –OH), 8.04 (d, *J* = 7.6 Hz, 1H, N=C–H), 7.43–7.30 (m, 4H, Ar–H), 7.23–7.21 (m, 2H, Ar–H), 7.09 (d, *J* = 7.6 Hz, 2H, Ar–H), 7.04 (t, *J* = 7.6 Hz, 1H, Ar–H), 2.94 (t, *J* = 6.4 Hz, 2H, CH_2), 2.71 (t, *J* = 7.2 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 186.62, 140.95, 140.55, 139.54, 134.04, 130.82, 128.62, 126.83, 125.75, 125.54, 121.86, 114.81, 104.17, 28.74, 26.71.

$C_6F_5N{=}CHC_4H_4(C_6H_4)OH$ (2c). Yield: 70%. ^{1}H NMR ($CDCl_3$): δ 11.95 (d, *J* = 10.3 Hz, 1H, –OH), 8.06 (d, *J* = 7.6 Hz, 1H, N=C–H), 7.49–7.42 (m, 2H, Ar–H), 7.37 (t, *J* = 10.4 Hz, 1H, Ar–H), 7.23–7.26 (m, 1H, Ar–H), 2.94 (t, *J* = 4.4 Hz, 2H, CH_2), 2.69 (t, *J* = 5.6 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 189.26, 142.41, 141.74, 140.09, 139.58, 137.64, 137.13, 134.45, 132.70, 128.09, 127.04, 117.36, 108.71, 29.54, 27.88.

Synthesis of aluminium complexes 3a–c

Synthesis of aluminium complex 3a $[(2,6\text{-}^{i}Pr_2C_6H_3)N{=}CHC_4H_4(C_6H_4)O]Al(CH_3)_2$. Into a stirred solution of $(2,6\text{-}^{i}Pr_2C_6H_3)N{=}CHC_4H_4(C_6H_4)OH$ (0.71 g, 2.15 mmol) in toluene (10 mL), $AlMe_3$ (1 M *n*-hexane solution, 2.2 mL) was added drop-wise over a 10 min period at −20 °C. The solution was allowed to warm to room temperature and was stirred for 3 h. The reaction mixture was concentrated *in vacuo*. The chilled-concentrated toluene and *n*-hexane mixture solution was placed in the freezer (−20 °C) and afforded complex **3a** (0.76 g, 95% yield) as yellow microcrystals. ^{1}H NMR ($CDCl_3$): δ 8.02 (d, *J* = 8.8 Hz, 1H, N=C–H), 7.42–7.32 (m, 4H, Ar–H), 7.25 (d, *J* = 3.2 Hz, 2H, Ar–H), 7.22–7.18 (m, 1H, Ar–H), 3.18–3.12 (m, 2H, –CH), 2.92 (t, *J* = 7.6 Hz, 2H, CH_2), 2.57 (t, *J* = 7.6 Hz, 2H, CH_2), 1.26 (d, *J* = 6.8 Hz, 6H, $–CH_3$), 1.09 (d, *J* = 6.8 Hz, 6H, $–CH_3$), −0.80 (s, 6H, Al–CH_3). ^{13}C NMR ($CDCl_3$): δ 171.78, 168.82, 143.54, 142.82, 140.81, 133.16, 131.60, 127.42, 126.89, 126.49, 124.04, 103.74, 28.87, 28.05, 25.90, 25.85, 22.91, −9.84. Anal. calcd for $C_{25}H_{32}AlNO$: C, 77.09; H, 8.28; N, 3.60. Found: C, 77.18; H, 8.24; N, 3.72.

Synthesis of aluminium complex 3b $[C_6H_5N{=}CHC_4H_4(C_6H_4)O]Al(CH_3)_2$. Synthesis of **3b** was carried out according to the same procedure as that of **3a**, except $(C_6H_5)N{=}CHC_4H_6(C_6H_4)OH$ (0.53 g, 2.15 mmol) was used. Yield 0.58 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.99 (d, *J* = 8.8 Hz, 1H, N=C–H), 7.75 (s, 1H, Ar–H), 7.42–7.37 (m, 4H, Ar–H), 7.34–7.31 (m, 3H, Ar–H), 7.25–7.20 (m, 2H, Ar–H), 2.92 (t, *J* = 6.8 Hz, 2H, CH_2), 2.64 (t, *J* = 6.8 Hz, 2H, CH_2), −0.72 (s, 6H, Al–CH_3). ^{13}C NMR ($CDCl_3$): δ 172.29, 165.19, 147.68, 140.97, 132.96, 131.67, 129.56, 127.39, 126.82, 126.46, 126.37, 121.87, 104.87, 28.84, 26.12, −9.21. Anal. calcd for $C_{19}H_{20}AlNO$: C, 74.74; H, 6.60; N, 4.59. Found: C, 74.61; H, 6.47; N, 4.54.

Synthesis of aluminium complex 3c $[C_6F_5N{=}CHC_4H_4(C_6H_4)O]Al(CH_3)_2$. Synthesis of **3c** was carried out according to the same procedure as that of **3a**, except $(C_6F_5)N{=}CHC_4H_6(C_6H_4)OH$ (0.73 g, 2.15 mmol) was used. Yield 0.75 g (88%). ^{1}H NMR ($CDCl_3$): δ 8.03 (d, *J* = 7.6 Hz, 1H, N=C–H), 7.47–7.43 (m, 2H, Ar–H), 7.37–7.33 (m, 1H, Ar–H), 7.25–7.23 (m, 1H, Ar–H), 2.96 (t, *J* = 6.8 Hz, 2H, CH_2), 2.64 (t, *J* = 6.8 Hz, 2H, CH_2), −0.79 (s, 6H, Al–CH_3). ^{13}C NMR ($CDCl_3$): δ 177.53, 167.49, 142.10, 141.07, 133.10, 132.37, 127.77, 127.34, 127.10, 126.22, 125.69, 123.04, 106.23, 28.79, 26.12, −10.74. Anal. calcd for

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

$C_{19}H_{15}AlF_5NO$: C, 57.73; H, 3.82; N, 3.54. Found: C, 57.61; H, 3.87; N, 3.54.

Synthesis of aluminium complexes 1 and 2

Synthesis of aluminium complex 1. Complex **1** was prepared according to literature procedures.[22]

Synthesis of aluminium complex 2. Synthesis of **2** was carried out according to the same procedure as that of **3a**, except (2,6-$^{i}Pr_2C_6H_3$)NC(CH_3)C(H)C(C_6H_5)OH (0.69 g, 2.15 mmol) was used. Yield 0.77 g, 95%. ^{1}H NMR ($CDCl_3$): δ 7.96–7.94 (m, 2H, Ar–H), 7.48–7.42 (m, 3H, Ar–H), 7.32–7.28 (m, 2H, Ar–H), 7.21–7.19 (m, 2H, Ar–H), 6.08 (s, 1H, CH), 3.02–2.96 (m, 2H, ^{i}Pr–CH), 1.91 (s, 3H, CO–CH_3), 1.22 (d, J = 6.8 Hz, 6H, ^{i}Pr–CH_3), 1.13 (d, J = 6.8 Hz, 6H, ^{i}Pr–CH_3), −0.86 (s, 6H, Al–CH_3). ^{13}C NMR ($CDCl_3$): δ 175.75, 173.30, 141.79, 138.21, 136.27, 130.08, 127.25, 126.19, 123.26, 96.57, 26.98, 23.60, 23.43, 22.83, −12.14. Anal. calcd for $C_{24}H_{32}AlNO$: C, 76.36; H, 8.54; N, 3.71. Found: C, 76.18; H, 8.62; N, 3.77.

X-Ray crystallography

Single crystals of complexes **3a–c** suitable for X-ray structure determination were grown from a concentrated CH_2Cl_2–hexane mixture solution at −30 °C in a glove box, thus maintaining a dry, O_2-free environment. The intensity data were collected with the ω scan mode (186 K) on a Bruker Smart APEX diffractometer with a CCD detector using Mo Kα radiation (λ = 0.71073 Å). Lorentz, polarization factors were made for the intensity data and absorption corrections were performed using the SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

Ring-opening polymerisation of ε-caprolactone

Typical polymerisation procedures (entry 4, Table 2) are as follows. Into a sealed Schlenk tube containing a toluene solution of **3a** (0.050 mmol), ^{i}PrOH (0.5 mL, 0.050 mmol) was added in a drybox at room temperature. The solution was stirred for 10 minutes, and then ε-CL (5.0 mmol) was added to the solution. The reaction mixture was then placed into an oil bath pre-heated at 80 °C, and the solution was stirred for the prescribed time (10 min). The polymerisation mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL) and collected as the methanol insoluble white precipitates. The resultant polymer was then collected on a filter paper and was dried *in vacuo*.

Ring-opening polymerisation of L-lactide

Typical polymerisation procedures (entry 13, Table 2) are as follows. Into a sealed Schlenk tube containing a toluene solution of **3c** (0.050 mmol), ^{i}PrOH (0.5 mL, 0.050 mmol) was added in a drybox at room temperature. The solution was stirred for 10 minutes, and then L-LA (5.0 mmol) was added to the solution. The reaction mixture was then placed into an oil bath pre-heated at 80 °C, and the solution was stirred for the prescribed time (4 h). The polymerisation mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL). The ring opened polymer was then collected as the methanol insoluble white precipitates; the resultant polymer was then collected on a filter paper and was dried *in vacuo*.

Synthesis of diblock copolymers

The same procedure is followed for all diblock copolymer syntheses. Typical polymerisation procedures (entry 1, Table 3) are as follows. Into a sealed Schlenk tube containing a toluene solution of **3a** (0.050 mmol), ^{i}PrOH (0.5 mL, 0.050 mmol) was added in a dry box at room temperature. The solution was stirred for 10 minutes, and then ε-CL (5.0 mmol) was added to the solution. The reaction mixture was then placed into an oil bath pre-heated at 80 °C, and the solution was stirred for the prescribed time (5 min). Subsequently, the second monomer L-LA (5.0 mmol) was added to the polymerisation mixture and heated at the same temperature. The polymerisation was continued for the prescribed time (4 h). The polymerisation mixture was then quenched by adding methanol (1.0 mL), and the resultant solution was then poured into methanol (400 mL). The ring opened polymer was then collected as the methanol insoluble white precipitates; the resultant polymer was then collected on a filter paper and was dried *in vacuo*.

Acknowledgements

The authors are grateful for financial support provided by the National Natural Science Foundation of China (no. 20923003).

References

1 J. C. Wu, T. L. Yu, C. T. Chen and C. C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602–626.
2 O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.
3 L. S. Nair and C. T. Laurencin, *Prog. Polym. Sci.*, 2007, **32**, 762–798.
4 A. Arbaoui and C. Redshaw, *Polym. Chem.*, 2010, **1**, 801–826.
5 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841–1846.
6 Y. Shen, K. J. Zhu, Z. Shen and K. M. Yao, *J. Polym. Sci., Part A: Polym. Chem.*, 1996, **34**, 1799–1805.
7 J. M. Vion, R. Jérôme, P. Teyssie, M. Aubin and R. E. Prudhomme, *Macromolecules*, 1986, **19**, 1828–1838.
8 Y. Wang and H. Y. Ma, *Chem. Commun.*, 2012, **48**, 6729–6731.
9 N. Nomura, A. Akita, R. Ishii and M. Mizuno, *J. Am. Chem. Soc.*, 2010, **132**, 1750–1751.
10 G. Li, M. Lamberti, D. Pappalardo and C. Pellecchia, *Macromolecules*, 2012, **45**, 8614–8620.

 This journal is © The Royal Society of Chemistry 2014

Published on 18 November 2013. Downloaded by University of Southern California on 01/04/2014 11:45:14.

11 J. K. Kim, D. J. Park, M. S. Lee and K. J. Ihn, *Polymer*, 2001, **42**, 7429–7441.
12 P. J. A. IntVeld, E. M. Velner, P. V. D. Witte, J. Hamhuis, P. J. Dijkstra and J. Feijen, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 219–226.
13 M. H. Huang, S. M. Li, J. Coudane and M. Vert, *Macromol. Chem. Phys.*, 2003, **204**, 1994–2001.
14 A. C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466–1486.
15 J. L. Wang and C. M. Dong, *Macromol. Chem. Phys.*, 2006, **207**, 554–562.
16 H. R. Kricheldorf, K. Bornhorst and H. Hachmann-Thiessen, *Macromolecules*, 2005, **38**, 5017–5024.
17 F. Stassin and R. Jérôme, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 2777–2789.
18 M. Florczak, J. Libiszowski, J. Mosnacek, A. Duda and S. Penczek, *Macromol. Rapid Commun.*, 2007, **28**, 1385–1391.
19 D. Pappalardo, L. Annunziata and C. Pellecchia, *Macromolecules*, 2009, **42**, 6056–6062.
20 D. Dakshinamoorthy and F. Peruch, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2161–2171.
21 N. Nomura, T. Aoyama, R. Ishii and T. Kondo, *Macromolecules*, 2005, **38**, 5363–5366.
22 J. Y. Liu, N. Iwasa and K. Nomura, *Dalton Trans.*, 2008, 3978–3988.
23 N. Iwasa, J. Y. Liu and K. Nomura, *Catal. Commun.*, 2008, **9**, 1148–1152.
24 W. J. Zhang, Y. H. Wang, J. Cao, L. Wang, Y. Pan, C. Redshaw and W. H. Sun, *Organometallics*, 2011, **30**, 6253–6261.
25 M. Shen, W. Huang, W. J. Zhang, X. Hao, W. H. Sun and C. Redshaw, *Dalton Trans.*, 2010, **39**, 9912–9922.
26 K. F. Peng and C. T. Chen, *Dalton Trans.*, 2009, 9800–9806.
27 R. C. Yu, C. H. Hung, J. H. Huang, H. Y. Lee and J. T. Chen, *Inorg. Chem.*, 2002, **41**, 6450–6455.
28 W. Y. Li, W. T. Wu, Y. R. Wang, Y. M. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2011, **40**, 11378–11381.
29 T. L. Huang and C. T. Chen, *J. Organomet. Chem.*, 2013, **725**, 15–21.
30 A. Arbaoui, C. Redshaw and D. L. Hughes, *Chem. Commun.*, 2008, 4717–4719.
31 J. Koller and R. G. Bergman, *Organometallics*, 2011, **30**, 3217–3224.
32 M. Bouyahyi, T. Roisnel and J. F. Carpentier, *Organometallics*, 2012, **31**, 1458–1466.
33 H. L. Chen, S. Dutta, P. Y. Huang and C. C. Lin, *Organometallics*, 2012, **31**, 2016–2025.
34 Y. C. Liu, B. T. Ko and C. C. Lin, *Macromolecules*, 2001, **34**, 6196–6201.
35 M. Lamberti, I. D. Auria, M. Mazzeo, S. Milione, V. Bertolasi and D. Pappalardo, *Organometallics*, 2012, **31**, 5551–5560.
36 L. Postigo, M. C. Maestre, M. E. G. Mosquera, T. Cuenca and G. Jiménez, *Organometallics*, 2013, **32**, 2618–2624.
37 M. Normand, V. Dorcet, E. Kirillov and J. F. Carpentier, *Organometallics*, 2013, **32**, 1694–1709.
38 I. W. Hamley, V. Castelletto, R. V. Castillo, A. J. Müller, C. M. Martin, E. Pollet and P. Dubois, *Macromolecules*, 2005, **38**, 463–472.
39 I. W. Hamley, P. Parras, V. Castelletto, R. V. Castillo, A. J. Müller, E. Pollet, P. Dubois and C. M. Martin, *Macromol. Chem. Phys.*, 2006, **207**, 941–953.
40 D. P. Song, J. Q. Wu, W. P. Ye, H. L. Mu and Y. S. Li, *Organometallics*, 2010, **29**, 2306–2314.