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Crystallographic characterisation of novel Zn(II) silsesquioxane complexes and their application as initiators for the production of polylactide

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ABSTRACT

Herein, the solid state structures of the products from the reaction of the silsesquioxane triol (*iso*-$C_4H_9)_7Si_7O_{12}(OH)_3$ (**1**) with two equivalents of $ZnMe_2$ in both THF and toluene are reported. In both cases tetrametallic Zn(II) complexes were isolated, with toluene $[($*iso*-$C_4H_9)_7Si_7O_{12}]_2Zn_4Me_2$ (**2**) was prepared while performing the reaction in THF the analogous complex $[($*iso*-$C_4H_9)_7Si_7O_{12}]_2Zn_4Me_2(THF)_2$ (**3**) was formed. Both species have also been characterised *via* ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectroscopy, which confirm the solid state structures are maintained in solution. Both **2** and **3** show modest activities for the polymerisation of *rac*-lactide and a heterogeneous catalyst has also been prepared.

1. Introduction

It is known that silsesquioxanes can be used as models for silica surfaces and major advances in this area and general silsesquioxane coordination chemistry have been achieved [1–5]. For example, Johnson and Crocker have prepared titanium silsesquioxanes as models for heterogeneous epoxidation catalysts [6–8]. We have recently utilised Ti(IV) and Al(III) silsesquioxane complexes as models for heterogeneous initiators for polylactide production [9]. This paper details the preparation and characterisation of two silsesquioxane complexes based on Zn(II) and the single crystal X-ray structure of the parent trisilanol. To the best of our knowledge (from the Cambridge structural data base) only one crystallographically characterised Zn(II) silsesquioxane has been reported [10]. In this example, a Zn–Me complex of the silsesquioxanedisilanol (c-$C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ was described [11]. Hitherto, there are no literature reports of crystallographically characterised examples of the reaction of the silsesquioxanetrisilanol family with a $Zn(alkyl)_2$ [10]. However, an analogous tetranuclear magnesium silsesquioxane complex has been prepared by the reaction of the triol with methylmagnesium chloride [12]. Other examples of silsesquioxane metal complexes include aluminium [13–17], vanadium [18], tin [19], gallium [15], molybdenum [20] and group 4 metals [21–24].

There is continued interest in the coordination chemistry of silsesquioxanes and the use of these as soluble models for homogeneous catalysts. Therefore, in this paper we report the full characterisation of two novel Zn(II) silsesquioxane complexes prepared by reacting one equivalent of triol **1** with two equivalents of $ZnMe_2$ in toluene (**2**) or THF (**3**) as the solvent (Scheme 1). The results of which will be compared to a heterogeneous system.

2. Results and discussion

The molecular structure of the parent silsesquioxane (*iso*-$C_4H_9)_7Si_7O_{12}(OH)_3$ (**1**) was determined and is shown in Fig. 1. This was previously reported by Feher, however, no discussion of metric data was presented due to the quality of the data set [25].

The bond lengths and angles are in agreement with previously reported triol silsesquioxanes in the literature [26,27]. Recently, Unno and co-workers have reported the structure of **1**, which is analogous (in respect to metric data including H-bonding) to that reported herein [28]. One equivalent of **1** was treated with two equivalents of $ZnMe_2$ in toluene, recrystallisation in hexane yielded crystals of **2** upon standing at room temperature (see Fig. 2). Complex **2** is a tetranuclear zinc compound with two chemically distinct zinc centres {Zn(1) and Zn(2)} and **2** is soluble in common organic solvents such as CH_2Cl_2, THF and toluene. There is a crystallographic centre of inversion in the molecule and **2** crystallises in the triclinic space group $P\bar{1}$. The four zinc centres form an interlayer between two trianionic silsesquioxane units. There are three planar four membered rings (two zinc and two oxygen centres) present. The central ring {Zn(2), Zn(2A), O(13), O(13A)} is almost perpendicular to the two outer rings, with the angle between the planes formed from Zn2A–O13–Zn2–O13A and Zn2–O2–Zn1–O5A being 87°. Zn(1) is bound to two oxygen moieties {O(2) and O(5A)} and the methyl group C(1), with the metric data for Zn(1) being in agreement with the only previously crystallographically characterised Zn–silsesquioxane complex in the literature (see

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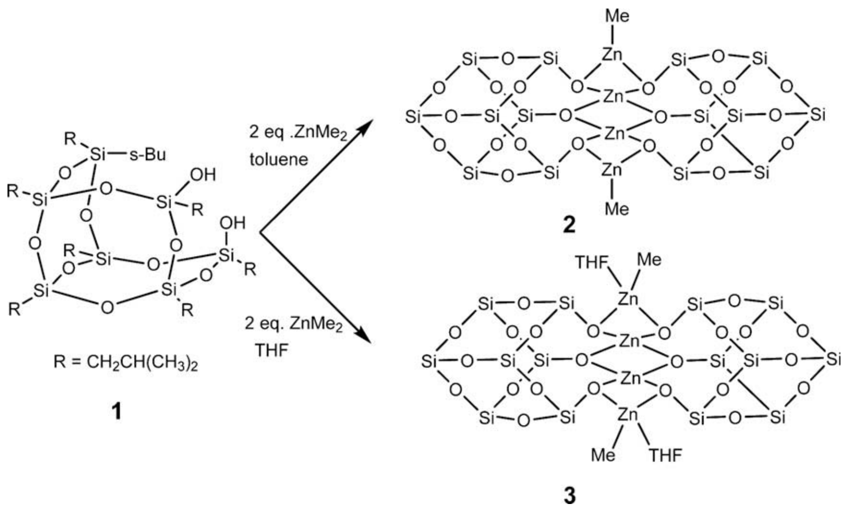

Scheme 1. Zn(II) silsesquioxane complexes prepared in this study.

Table 1) [11]. Zn(1) is in an extremely distorted trigonal planar geometry, as exemplified by the O(2)–Zn(1)–C(1) 139.70(18)°, O(5A)–Zn(1)–C(1) 135.60(18)° and O(2)–Zn(1)–5(A) 84.64(11)° angles. The Zn(1)–C(1) distance of 1.922(5) Å, is in agreement with the literature precedent [29,30]. Zn(2) is bound to four oxygen centres and has a distorted tetrahedral geometry, which is exemplified by the angles O(13)–Zn(2)–O(13A) 87.71(11)° and O(13)–Zn(2)–O(2) 120.70(10)°. The central metallic core in **2** is different to that produced from the reaction of $(c\text{-}C_5H_9)_7Si_7O_9(OSiMePh_2)(OH)_2$ with $Zn(Me)_2$ where one of the oxygen moieties is bound to three Zn-centres and all Zn(II) centres remain coordinated to a methyl group, which is not the case in this example [11]. The metallic core of **2** is analogous to that of Mg(II)–$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ complex [12]. In solution the $^{29}Si\{^1H\}$ NMR spectrum (C_6D_6) shows five resonances in a 2:1:1:2:1 ratio which is consistent with the solid state structure being maintained in solution. In the ^1H NMR spectrum a singlet at −0.12 ppm was detected, characteristic for the Zn–Me resonance, this was further confirmed *via* a sharp singlet at −15.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum [11,30].

When the same reaction was performed in THF complex **3** (Fig. 3) was isolated, which is highly soluble in THF, toluene and hexane. Crystals suitable for X-ray diffraction were obtained by cooling (−20 °C) a saturated solution of **3** in hexane. Complex **3** also crystallises in the triclinic space group $P\bar{1}$. Again a tetranuclear arrangement of Zn(II) is observed with three Zn_2O_2 rings. These rings are more puckered than in **2**, this is exemplified by the angle between the Zn2–O5A–O2 and O2–Zn1–O5A planes of 161° *cf.* 177° for the analogous angle in **2**. Zn(1) has a highly distorted tetrahedral geometry which is illustrated by the following O(2)–Zn(1)–C(1) 131.17(14)° and O(2)–Zn(1)–O(1) 97.76(10)°. The O_{sil}–Zn(1) distances are significantly longer in **3** than **2** (O_{sil}–Zn av. 2.018 Å *cf.* 1.957 Å for **2**) due to the coordinated THF molecule. Zn(2) sits in a distorted tetrahedral environment, analogous to **2**. Again the solution ^1H and $^{13}C\{^1H\}$ NMR spectra clearly show resonances for the Zn–Me moiety (−0.18 ppm in the ^1H NMR and −15.6 ppm in the $^{13}C\{^1H\}$ NMR). The $^{29}Si\{^1H\}$ NMR has five resonances in a 2:1:1:2:1 ratio indicating that the structure is maintained in solution. The metric data for **2** and **3** are summarised in Table 1.

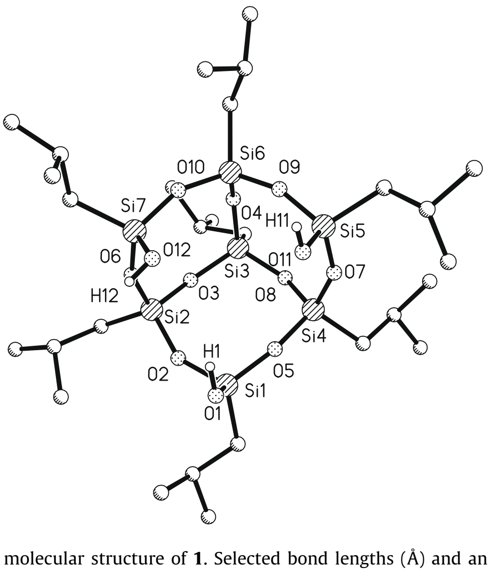

Fig. 1. The molecular structure of **1**. Selected bond lengths (Å) and angles (°) are Si(1)–O(1) 1.6293(16), Si(1)–O(2) 1.6205(18), Si(1)–O(5) 1.6143(17), Si(4)–O(5) 1.6133(17), Si(4)–O(7) 1.6190(18), Si(4)–O(8) 1.6190(18), O(2)–Si(1)–O(5) 110.34(9), O(2)–Si(1)–O(1) 108.92(10). Hydrogen atoms not involved in hydrogen bonding have been removed for clarity.

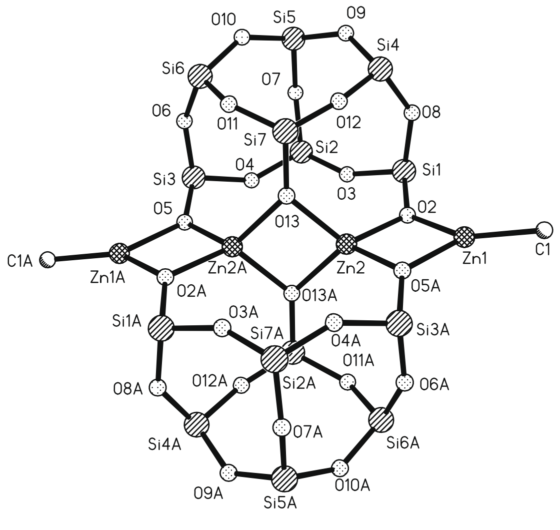

Fig. 2. The molecular structure of **2**. The *iso*-butyl groups and hydrogen atoms have been omitted for clarity. Labels with suffix A relate to those in the asymmetric unit by the −*x*, − *y* + 2, −*z* symmetry operation.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **2** and **3**.

	2	3
Zn(1)–O(1)		2.127(3)
Zn(1)–C(1)	1.923(5)	1.951(4)
Zn(1)–O(2)	1.954(3)	2.015(2)
Zn(1)–O(5A)	1.959(3)	2.021(2)
Zn(2)–O(2)	1.956(3)	1.949(2)
Zn(2)–O(13)	1.959(3)	1.946(2)
Zn(2)–O(13A)	1.951(3)	1.984(2)
Zn(2)–O(5A)	1.946(3)	1.961(2)
O(1)–Zn(1)–C(1)		107.42(14)
O(2)–Zn(1)–C(1)	139.71(18)	131.17(14)
O(2)–Zn(1)–O(5A)	84.65(11)	83.06(8)
O(1)–Zn(1)–O(2)		97.76(10)
O(13)–Zn(2)–O(2)	120.69(10)	123.43(8)
O(13)–Zn(2)–O(5A)	119.41(12)	129.48(9)

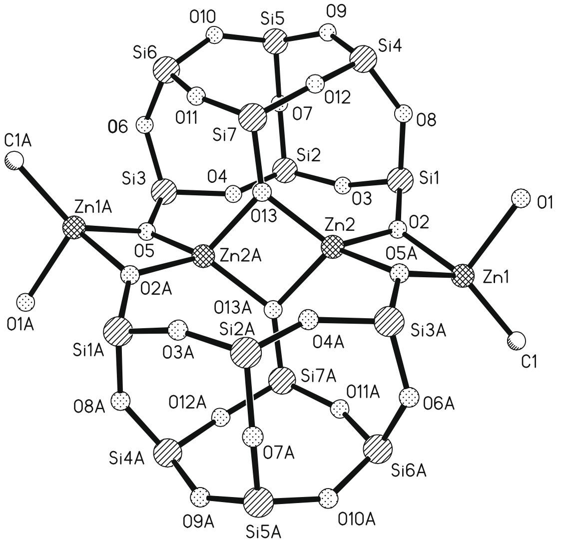

Fig. 3. The molecular structure of **3**. The *iso*-butyl groups, hydrogen atoms and the carbons of the THF moiety have been omitted for clarity. Labels with suffix A relate to those in the asymmetric unit by the $-x$, $-y+1$, $-z+1$ symmetry operation.

Table 2
Polymerisation data.

Initiator	Yield[a]	M_w[b]	PDI[b]	P_r[c]
2	15	2400	1.08	0.5
3	10	1900	1.12	0.5
Heterogeneous	10	1800	1.08	0.5

[a] Isolated yield.

[b] Determined from GPC measurements (THF at 1 ml per minute, relative to polystyrene standards).

[c] Calculated from analysis of the methine region of the ^{1}H homonuclear decoupled spectrum.

Zn(II) complexes have found great utility as initiators for the production polylactide (PLA) [31–36]. Heterogeneous catalysts are finding utility in the area of ring opening polymerisation (ROP) initiators for PLA [9,37–40]. A heterogeneous initiator was prepared by treating a silica surface with $ZnMe_2$, in an analogous fashion to the soluble silsesquioxane complexes **2** and **3**. Complexes **2**, **3** and the heterogeneous system were trialled for the ROP of *rac*-lactide in toluene (*iso*-propyl alcohol was added to generate the Zn–O^{i}Pr *in situ*, see Section 4). Modest conversions were obtained after prolonged reaction time (Table 2). The polymers produced had low PDIs and from analysis of the methine region of the ^{1}H NMR spectra were all atactic. A blank run with pure SiO_2 failed to produce polymer under analogous conditions.

3. Conclusions

In conclusion two novel Zn–silsesquioxane complexes are reported. Both complexes have a tetrameric zinc layer with two capping silsesquioxanes. The complexes have been used as homogeneous initiators for the ring opening polymerisation of *rac*-lactide and a heterogeneous catalyst has been prepared for comparison.

4. Experimental

4.1. General procedures

^{1}H, ^{13}C{^{1}H}and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker 500 MHz spectrometer, and referenced to residual solvent peaks of C_6D_6 which was dried prior to use. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A.K. Carver at the Department of Chemistry, University of Bath. In all cases the yields quoted are for those of the crystalline material. Both **2** and **3** decomposed before they melted.

4.2. X-ray crystallography

All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs [41]. All hydrogen atoms, were included in idealised positions and refined using the riding model. For both **2** and **3** the ADPs for the carbons of the *iso*-butyl groups are slightly less isotropic than desirable, where appropriate these have been modelled. For **3** the *iso*-butyl groups adoring Si(2), Si(3) and Si(5) were modelled over two sites, in all cases a 50:50 model provided the best convergence. In the case of **2** it was slightly more complex with the carbons of the *iso*-butyl groups of the following silicon sites being disordered Si(1) {55:45}, Si(2) {65:35}, Si(3) {60:40}, Si(5) {50:50}, Si(6) {80:20} with the numbers in brackets representing the occupancy that afforded the best convergence. For the pure *iso*-butyl trisilanol **1** the *iso*-butyl group from Si(6) was disordered in a 65:35 occupancy. Multi-scan absorption corrections were applied where appropriate.

4.3. Synthesis and characterisation of *1–3*

During the course of this work the crystal structure of the free silsesquioxane was determined: Crystal data for **1**: $C_{28}H_{66}O_{12}Si_7$, $M = 791.44$, $0.20 \times 0.20 \times 0.20$ mm^3, monoclinic, space group $P2_1/n$, $a = 14.102(1)$ Å, $b = 21.335(2)$ Å, $c = 14.748(1)$ Å, $\beta = 100.072(1)°$, $V = 4368.79(6)$ Å^3, $Z = 4$, $D_c = 1.203$ g cm^{-3}, $F_{000} = 1712$, Mo Kα radiation, $2\theta_{max} = 55.0°$, 77 415 reflections collected, 10 008 unique ($R_{int} = 0.0396$). Final $GooF = 1.130$, $R_1 = 0.0467$, $wR_2 = 0.1187$, R indices based on 8672 reflections with $I > 2\sigma(I)$ (refinement on F^2), 468 parameters, 0 restraints, $\mu = 0.268$ mm^{-1}.

4.3.1. Preparation of [(iso-C_4H_9)$_7Si_7O_{12}$]$_2Zn_4Me_2$ (*2*)

1 (1.57 g, 2 mmol) was dissolved in toluene (20 ml). To this $ZnMe_2$ (2 ml, 2 M solution in toluene, 4 mmol) was added, there was vigorous effervescence. The mixture was stirred at room temperature for 1 h. After which time the toluene was removed *in vacuo* and the white solid was recrystallised in the minimum amount of hexane. This was left at room temperature and after 24 h crystals suitable for X-ray diffraction were obtained, yield 0.95 g 50%. ^{1}H (C_6D_6) −0.12 (6H, s, Zn–CH_3), 0.77–0.99 (28H, m, $SiCH_2$), 1.02–1.34 (84H, m, CH_3), 2.02–2.30 (14H, m, CH). ^{13}C{^{1}H} (C_6D_6) −15.7 (Zn–CH_3), 22.9, 23.2 (CH_2), 24.4 (CH_2), 24.4, 24.5, 24.6 (CH), 24.7 (CH_2), 24.8 (CH), 24.9 (CH_2), 25.9, 26.1, 26.2, 26.2, 26.4, 26.6, 26.7 (CH_3). ^{29}Si{^{1}H} (C_6D_6) −57.7, −62.5, −64.9, −65.3, −70.3 (2:1:1:2:1 ratio). Elemental analysis: *Anal.* Calc. for $C_{58}H_{132}Zn_4O_{24}Si_{14}$: C, 37.28; H, 7.12. Found: C, 37.3; H, 6.94%. Crystal data for **2**: $C_{29}H_{66}O_{12}Si_7Zn_2$, $M = 934.19$, $0.20 \times 0.15 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 13.7070(5)$ Å, $b = 14.1560(7)$ Å, $c = 14.3980(8)$ Å, $\alpha = 71.362(2)°$, $\beta = 68.977(2)°$, $\gamma = 62.959(3)°$, $V = 2281.18(19)$ Å^3, $Z = 2$, $D_c = 1.360$ g cm^{-3}, $F_{000} = 988$, $2\theta_{max} = 50.3°$, 21 134 reflections collected, 7987 unique ($R_{int} = 0.0664$). Final $GooF = 1.042$, $R_1 = 0.0485$, $wR_2 = 0.0994$, R indices based on 5347 reflections with $I > 2\sigma(I)$ (refinement on F^2), 640 parameters, 0 restraints, $\mu = 1.285$ mm^{-1}.

4.3.2. Preparation of [(iso-C_4H_9)$_7$$Si_7O_{12}$]$_2$$Zn_4Me_2THF_2$ (**3**)

1 (1.57 g, 2 mmol) was dissolved in THF (20 ml). To this $ZnMe_2$ (2 ml, 2 M solution in toluene, 4 mmol) was added, there was vigorous effervescence. The mixture was stirred at room temperature for 1 h. After which time the THF was removed *in vacuo* and the white solid was recrystallised in the minimum amount of hexane. This was left at −20 °C and after several weeks crystals suitable for X-ray diffraction were obtained, yield 0.85 g, 43%. ^{1}H (C_6D_6) −0.18 (6H, s, Zn–CH_3), 0.76–0.98 (28H, m, $SiCH_2$), 1.05–1.40 (84H, m, CH_3), 1.53 (8H, br m, CH_2 THF), 2.03–2.30 (14H, m, CH), 3.82 (8H, br m, CH_2 THF). ^{13}C{^{1}H} (C_6D_6) −15.6 (Zn–CH_3), 23.0, 23.5 (CH_2), 24.5, 24.5, 24.6 (CH), 24.6 (CH_2), 24.7 (CH_2), 24.8 (CH), 25.1 (CH_2), 25.5 (CH_2 THF), 26.0, 26.2, 26.2, 26.3, 26.5, 26.7, 26.8 (CH_3), 68.8 (O–CH_2 THF). ^{29}Si{^{1}H} (C_6D_6) −58.1, −62.9, −64.9, −65.1, −70.4 (2:1:1:2:1 ratio). Elemental analysis: *Anal.* Calc. for $C_{66}H_{148}Zn_4O_{26}Si_{14}$: C, 39.39; H, 7.41. Found: C, 38.9; H, 7.01%. Crystal data for **3**: $C_{33}H_{74}O_{13}Si_7Zn_2$, $M = 1006.29$, colourless block, $0.20 \times 0.10 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$, $a = 12.0510(2)$ Å, $b = 15.3660(3)$ Å, $c = 16.2700(3)$ Å, $\alpha = 64.086(1)°$, $\beta = 70.202(1)°$, $\gamma = 70.672(1)°$, $V = 2489.41(8)$ Å^3, $Z = 2$, $D_c = 1.342$ g cm^{-3}, $F_{000} = 1068$, $2\theta_{max} = 55.0°$, 49 676 reflections collected, 11 359 unique ($R_{int} = 0.0961$). Final $GooF = 1.012$, $R_1 = 0.0468$, $wR_2 = 0.1035$, R indices based on 7550 reflections with $I > 2\sigma$(I) (refinement on F^2), 616 parameters, 0 restraints, $\mu = 1.184$ mm^{-1}.

4.3.3. Preparation of SiO_2–Zn–Me

Sixty angstrom silica (2.0 g) was dried at 130 °C under a dynamic vacuum for 24 h. To this hexane (20 ml) was added and $ZnMe_2$ (2 M in toluene, 3 ml, 6 mmol) was slowly added. Vigorous effervescence was observed and the solution was left for 2 h. The solution was filtered and the white solid washed with toluene (2 × 25 ml) and hexane (2 × 25 ml) and dried *in vacuo*. The white solid was stored in a glove-box and used as required.

4.4. Polymerisation procedure

The monomer *rac*-lactide (0.72 g, 5 mmol) was added to a Schlenk flask to which toluene {20 ml containing 2 equivalents of *iso*-propyl alcohol (IPA)} was added. The initiator **2** (47 mg) or **3** (50 mg) was then added so that the monomer:initiator:IPA was 100:1:2. In the case of the heterogeneous catalyst 50 mg of material was used. The mixture was heated at 110 °C for 72 h, after this time the flask was cooled and the solvent removed *in vacuo*. The residue was washed with MeOH (3 × 50 ml) and the residue was dried. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra, the equations used to calculate P_r and P_m are given by Coates et al. [32]. Gel permeation chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 µm MIXED-D 300 × 7.5 mm column at 35 °C, THF solvent (flow rate, 1.0 ml/min). The polydispersity index (PDI) was determined from M_w/M_n, where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615–568 000 Da. For PLA the M_n values obtained from GPC are typically higher than expected due to the hydrodynamic volume difference between PLA and the polystyrene standards [42].

Supplementary data

CCDC 711114–711116 contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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