UNIVERSITY OF BATH

University of Bath

1

Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate)

Michael R. Kember, James Copley, Antoine Buchard and Charlotte K. Williams*

Graphical abstract image

Please check this proof carefully. **Our staff will not read it in detail after you have returned it**.

Translation errors between word-processor files and typesetting systems can occur so the whole proof needs to be read. Please pay particular attention to: tabulated material; equations; numerical data; figures and graphics; and references. If you have not already indicated the corresponding author(s) please mark their name(s) with an asterisk. Please e-mail a list of corrections or the PDF with electronic notes attached – do not change the text within the PDF file or send a revised manuscript.

Please bear in mind that minor layout improvements, e.g. in line breaking, table widths and graphic placement, are routinely applied to the final version.

We will publish articles on the web as soon as possible after receiving your corrections; no late corrections will be made.

Please return your **final** corrections, where possible within **48 hours** of receipt by e-mail to: polymers@rsc.org

Reprints—Electronic (PDF) reprints will be provided free of charge to the corresponding author. Enquiries about purchasing paper reprints should be addressed via: http://www.rsc.org/publishing/journals/guidelines/paperreprints/. Costs for reprints are below:

Reprint costs

No of pages	Cost (per 50 copies)	
	First	Each additional
2–4	£225	£125
5–8	£350	£240
9–20	£675	£550
21–40	£1250	£975
>40	£1850	£1550

Cost for including cover of journal issue:
£55 per 50 copies

Dynamic Article Links ▶

PAPER

Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate)†

Michael R. Kember, James Copley, Antoine Buchard and Charlotte K. Williams*

The preparation of α,ω-hydroxy-telechelic poly(cyclohexene carbonate) from a dizinc catalyst is reported. The telechelic polymer, with an yttrium initiator, can be used to polymerize lactide, yielding new triblock copolymers, substantially derived from renewable resources.

There is currently considerable economic and environmental interest in the development of methods to use renewable resources to make monomers and polymers.[1] Using biomass as a feedstock is attractive, there are already various commercial polymers, deriving from high starch content plants, possessing suitable properties for use as packaging materials, fibres and commodity plastics.[1a–g] Notable examples include poly(lactide), PLA, poly(hydroxy alkanoates) and derivatives of starch/cellulose.[1a–h,2] A critical factor controlling the adoption of such polymers is the development of efficient syntheses of both monomers and polymers. The ring-opening polymerization of lactones, derived from renewable resources, is an attractive synthetic route as judicious choice of initiator/conditions allows excellent polymerization control, facile access to high/low molecular weight products, stereocontrol and the production of block copolymers, considerably broadening the materials property profile.[3]

The copolymerization of carbon dioxide with epoxides also enables the partial replacement of petrochemicals, including toxic reagents such as phosgene, with a highly abundant, inexpensive, low toxicity feedstock.[4] It should be noted that only partial petrochemical substitution can be achieved in most cases, although the copolymerization of limonene oxide/CO_2 has been reported.[4d] The copolymerization is critically dependent on the selection of catalyst, not least so as to enable high degrees of polymerization control and CO_2 uptake.[4a–d] The development of controlled catalysts is important as it enables the production of block copolymers which show a wide range of properties.[5] Also highly significant has been the development of immortal polymerization catalysts, first reported by Inoue using aluminium porphyrins.[6] In immortal polymerizations the catalyst undergoes rapid and reversible chain transfer reactions with protic compounds (*e.g.* water, alcohols, acids).[7] An important feature of this type of polymerization is that the numbers of polymer chains, and the molecular weights, depend on both the number of molecules of catalyst and of chain transfer agent.

Since the initial reports of heterogeneous catalysts, developed from the hydrolysis of organo-zinc reagents, attention has focussed on zinc catalysts, including zinc phenolates, carboxylates, β-diiminate complexes and, more recently, deliberately targeted di-zinc complexes.[8] Metal(III) porphyrin complexes, including those of Cr, Co and Al, have also shown promise.[6,9] Another important class of CO_2/epoxide copolymerization catalysts are Co(III)/Cr(III) Schiff base (Salen) complexes, and their derivatives, as they show excellent rates, stabilities and high degrees of polymerisation control.[4a, 5b, 9d, 10] We are particularly interested in the development of block copolymers from CO_2/epoxide coupling reactions due to the possibility to prepare new polymer materials and architectures. In this context, there are a number of interesting reports of metal Schiff base catalysts, including their application in terpolymerizations using various epoxides and carbon dioxide.[10a, 11] Lee, and co-workers have also reported an immortal cobalt Schiff base catalyst which, in combination with various macro-initiators, can be used to prepare a range of di- and tri-block copolymers with poly(propylene carbonate).[7,11a] Very recently, Coates and co-workers reported the preparation of multi-block copolymers, including a pentablock, *via* sequential monomer addition and using a zinc β-diiminate catalyst.[12]
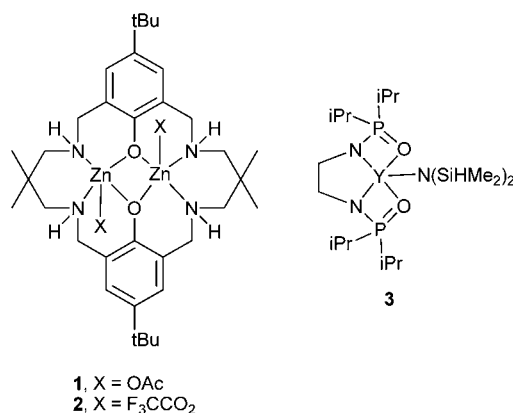

Fig. 1 CHO/CO_2 copolymerization catalysts **1** and **2**, and lactide ROP catalyst **3**.

Department of Chemistry, Imperial College London, London, SW7 2AZ, UK. E-mail: c.k.williams@imperial.ac.uk; Tel: +(0)20 795 4790
† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c2py00543c/

Our research group have recently reported a range of metal catalysts, coordinated by a macrocyclic ancillary ligand (Fig. 1), which show promise for cyclohexene oxide/CO_2 copolymerization. In particular, they operate under mild conditions, at ambient pressure of carbon dioxide, and show good TON/TOF.[8g, 13] We were interested to apply these catalysts to prepare block copolymers, so as to explore the range of properties, additionally we were motivated to increase the proportion of renewable resource content in the resulting copolymers. In this context, combining the ring-opening polymerization of lactide, a bio-derivative, with the alternating copolymerization of CHO/CO_2 seemed an attractive topic. Previously, Luinstra has described blends of PLA and poly(propylene carbonate) (PPC), showing high degrees of transparency, good barrier properties and suitability for some commodity applications.[4g, 4h] Furthermore, Ree and co-workers, reported the application of heterogeneous zinc glutarate catalysts to prepare random copoly(ε-caprolactone-propylene carbonate) which was more rapidly enzymatically degraded than PPC.[14] This year, Lui *et al.*, reported the terpolymerization of lactide, PO and CO_2, however, the encoporation of lactide units was low (<10%), as was the CO_2 uptake.[15] Herein, we describe the application of efficient polymerization catalysts to enable the production of new triblock copolymers comprising lactide and cyclohexene carbonate.

Results and discussion

Synthesis and characterisation

We have previously reported a di-zinc catalyst 1, which showed a very good TON for the copolymerization of cyclohexene oxide (CHO) and CO_2, under mild conditions.[13e] Complex 1 is not, however, a suitable catalyst for the preparation of well-defined block copolymers as it yields poly(cyclohexene carbonate) with bimodal molecular weight distributions.[13e] MALDI-ToF analyses show that the higher molecular weight series are due to PCHC end-capped with hydroxyl groups, whilst the lower molecular weight series are due to PCHC chains end-capped with acetate and hydroxyl groups. Thus, using complex 1 immortal polymerization occurs, the hydroxyl terminated chains arise due to chain transfer reactions with protic impurities, most likely due to reactions with water and/or cyclohexan-1,2-diol. This mixture of chain end groups would contaminate and complicate any subsequent copolymer syntheses. In the course of catalyst development studies, complex 2 was prepared and it showed quite different chain end-groups, making it a suitable central (B) block in ABA type block copolymers with lactide.

Complex 2 was synthesized by stirring one equivalent of the pro-ligand,[13c,13e] with two equivalents of [$Zn(O_2CCF_3)_2$], in methanol for 16 h at 25 °C, after which the solvent was removed and the complex was dried, under vacuum, with a dessicant. Like complex 1 (Fig. 1),[13e] the ^1H NMR spectrum of 2 shows the methine and bridge methyl groups to be diastereotopic. Two resonances in the aromatic region and for the *tert*-butyl group are visible, illustrating the formation of a major and a minor isomer in solution (see Fig. S1, ESI†). The $^{19}F\{^1H\}$ NMR spectrum of the complex, in d_4-methanol, exhibited just one resonance, at −77.0 ppm, suggesting only one trifluoroacetate environment (see Fig. S2, ESI†). Elemental analysis results

agreed closely with calculated values. The LSIMS mass spectrum shows a peak at 793 amu, which corresponds to the species [$L^1Zn_2(O_2CCF_3)$]$^+$. The FT-IR spectrum of the complex shows the presence of the trifluoroacetate group, with a carbonyl stretching absorption at 1680 cm^{-1}.[16]

Copolymerization of CHO and CO_2

Complex 2 was tested as a catalyst for the copolymerization of cyclohexene oxide (CHO) and CO_2 under atmospheric pressure, at 80 °C. The conditions were selected because they gave the best compromise between activity and selectivity using catalyst 1.[13e] Complex 2 showed almost identical catalytic activity to 1, the TON increased marginally from 438 to 477, whilst the TOF increased very slightly from 18 to 20 h^{-1}. The introduction of an electron-withdrawing substituent (CF_3) on the carboxylate co-ligand does not appear to significantly influence the rate. This could be because the rates are dominated by propagating reactions, which are less affected by the nature of the carboxylate group. The PCHC produced has 98% carbonate linkages, and a slightly higher number-averaged molecular weight (M_n: 9200 g mol^{-1}) than that produced by 1 under the same conditions (M_n: 6200 g mol^{-1}), at similar conversion (47%), albeit with a broader PDI of 1.38. The glass transition temperature (T_g) was 88 °C, slightly below the literature value (∼110–120 °C),[17] due to the low molecular weight of the polymer. It was interesting to observe that MALDI-ToF analysis revealed only one polymer series, with hydroxyl terminal groups at both ends of the polymer (see Fig. S4). The di-hydroxyl end-capped chains are attributed to contamination by water, which acts as a chain transfer reagent. Analysis of the ^1H NMR spectrum of the copolymer concurs with MALDI-TOF, with only terminal methyne protons corresponding to a dihydroxyl terminated telechelic copolymer observed (see Fig. 2). The presence of acetate terminated groups was observed in the ^1H NMR of PCHC produced by 1 with
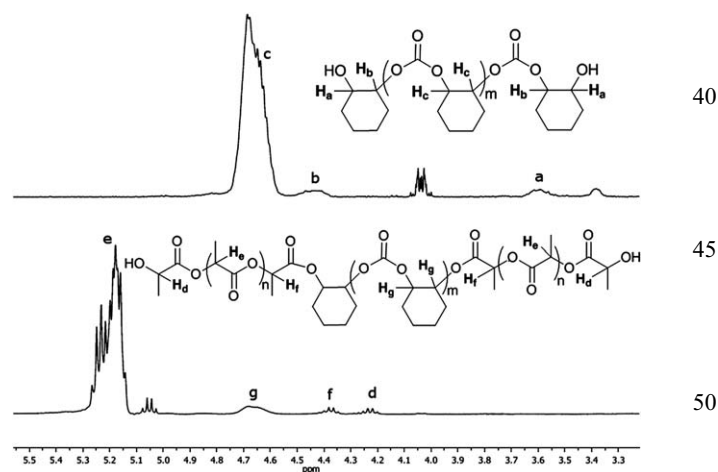
Fig. 2 ^1H NMR spectrum of PCHC (M_n = 9200 A, top) showing PCHC terminal (a, b) and core (c) methyne protons,[22] and PLA-PCHC-PLA (PCHC Mn = 2500, 100 equiv. *R,R*-lactide, B, bottom) showing core PCHC methyne protons (g) and PLA terminal (d), linkage (f) and core (e) methyne protons.[23] Resonance at 3.4 ppm in A corresponds to trace amounts of polyether linkages (<2%), resonance at 5.05 ppm in B corresponds to unreacted lactide.

ART ■ C2PY00543C

a resonance, due to the methyne protons on the terminal cylo-hexyl ring, at 4.3 ppm (see Fig. S4, ESI†). This resonance is absent in the copolymer produced by **2**.

Trifluoroacetate end groups are not observed for the PCHC samples prepared using **2** with either MALDI-TOF or NMR analysis, including by ^{19}F NMR spectroscopy. This is probably because they are more activated and, thus, undergo hydrolysis reactions more rapidly than acetate end-groups. The hydrolysis could occur either during the reaction, possibly catalyzed by the zinc complex, or during work-up. It is interesting to note the boiling point of trifluoroacetic acid (bp.78 °C) is lower than the reaction temperature, therefore, any liberated acid would be in the gas phase and thus chain transfer reactions might be slowed. In contrast, in the case of catalyst **1** any liberated acetic acid (bp. 118 °C) would be in the liquid phase and expected to be an efficient chain transfer agent.

The number-averaged molecular weight of the PCHC (9200 g mol^{-1}, at 47% conversion) implies that the average chain length is approximately 60 repeat units. Thus, there are approximately 8 chains produced per di-zinc catalyst (470/60), consistent with approximatley 0.8% by weight contamination with water. In comparison, a study by Duchateau and co-workers with zinc-β-diiminate catalysts found 2–6 chains per catalyst.[18] Initially, we considered that the incomplete drying of the zinc trifluoroacetate precursor could lead to contamination of the catalyst with water. However, elemental analysis of the complex shows an excellent fit with the experimental values, suggesting the maximum water content to be 0.2%, corresponding to 0.02% in the copolymeri-zation (as the loading of catalyst is 0.1%). Thermogravimetric analysis (TGA) also reveals very little weight loss at 100 °C. Therefore, the most likely sources of water are likely to be the monomer and/or carbon dioxide. Despite efforts to exclude water, including drying of the CHO (CaH$_2$), fractional distilla-tion and use of highest purity CO$_2$, the contamination remained at approx. 0.8% (vs. CHO). The production of copolymers with

lower than expected molecular weights, due to chain transfer reactions with contaminating water or other protic sources, is endemic to this copolymerisation.[13f] Many groups have reported low molecular weights, and bimodal weight distributions (as observed by GPC and MALDI-TOF MS), containing di-hydroxyl terminated copolymers.[9c,19] This is generally regarded as problematic; however, the selective formation of hydroxyl terminated telechelic polycarbonates is unusual and of high interest, particularly for use as a macroinitiator for ring-opening polymerisations (e.g. lactide) or coupling with di-isocyanates in the formation of polyurethanes.[7,20]

Block copolymerization of PCHC and lactide

PCHC has a moderate/high T$_g$ and the development of a unim-odal polymer series with two identical hydroxyl end groups presented an opportunity to combine PCHC with other bio-derived monomers to produce a block copolymer. Our research group have previously studied the yttrium amide complex (**3**) which, with exogenous alcohols, produces highly active and controlled lactide ring opening polymerization.[21] The telechelic PCHC ($M_n = 9200$ g mol^{-1}) was used as the added alcohol with complex **3** to produce an efficient initiating system for the ring-opening polymerization of lactide (200 eq. per OH group, 400 eq. total) yielding an ABA triblock copolymer.

The formation of a copolymer was confirmed by ^{1}H NMR spectroscopy, where resonances due to both blocks, were observed. We cannot rule out trace contamination of a diblock copolymer; however, the rate of chain transfer in such ring-opening polymerisations is well known to be significantly faster than propagation.[24] As both alcohol groups are in identical environments, the only expected product would be an ABA tri-block copolymer. In addition to this, ^{1}H NMR spectroscopy and MALDI-TOF do not indicate the presence of any mono-hydroxyl terminated PCHC in the starting material. We also did not observe any resonances in the ^{19}F{^{1}H} NMR spectrum of the polymer, indicating the absence of trifluoroacetate terminal groups. The resonances assigned to the terminal PCHC methyne protons (a and b, Fig. 2) were not observed in the tri-block copolymer, likely due to the deshielding by the adjacent ester group leading to them being masked by the PCHC resonances (g). We therefore propose that complete consumption of the terminal alcohol groups occurs and as the two hydroxyl terminal groups are in identical chemical environments that both groups react with highly oxophilic **3** at the same rate. This forms the active yttrium alkoxide species at each end of the copolymer, resulting in a triblock PLA-PCHC-PLA structure. Similarly, the use of large diols as macroinitiators for polymers of the form PLA-X-PLA has previously been reported with a variety of different groups.[23,25] Poly(lactide) terminal methyne protons were observed, with the resonance at 4.4 ppm assigned to the methyne proton within the linking PCHC-lactide unit (f), and the resonance at 4.2 ppm to the methyne protons within the terminal lactide unit (d).[23] Near complete conversion of the lactide was observed within 5 min of reaction, depending upon the loading of monomers (^{1}H NMR spectroscopy of the crude products revealed >95% conversion of lactide, in all cases). Gel Perme-ation Chromatography (GPC) analysis of the triblock copolymer showed a unimodal distribution with a molecular weight of
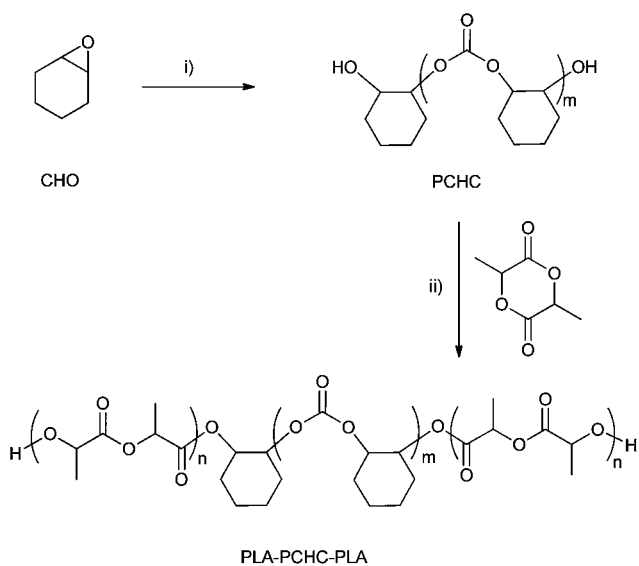
Scheme 1 Copolymerization of CHO and subsequent block copoly-merization with lactide. (i) **2** (0.1 mol %), 80 °C, 1 atm CO$_2$, 24 h. (ii) **3** (2 eq.), THF, 25 °C, 5 min.

51,000 g mol^{-1} (PDI = 1.30), and crucially, no signal was observed at lower weight, signifying the complete consumption of PCHC and formation of exclusively the PLA-PCHC-PLA triblock copolymer (see Figs. S7 and 3)

Using telechelic PCHC of molecular weight 9200 g mol^{-1}, polylactide chains were initiated, using 100–400 total equivalents of *rac*-lactide (50–200 equivalents of *rac*-lactide per chain end, entries 1–3, Table 1). The PCHC macroinitiator chain length was also varied, by quenching the copolymerization of CHO and CO_2 at shorter times (lower conversions), producing PCHC chains with M_n(GPC) of 6000 and 2500 g mol^{-1} (entries 5 and 6). Using these shorter telechelic macroinitiators and 200 equivalents of lactide (100 equivalents of lactide per chain end), enabled preparation of further ABA triblock copolymers. Two experiments were conducted using *S,S*-lactide, instead of *rac*-lactide, for comparison (entries 4 and 7, *cf.* entries 3 and 6 with *rac*-lactide). In all the experiments, the GPC analysis of the copolymers showed complete conversion of the PCHC and quantitative formation of the block copolymer (see Fig. 3). ^{1}H NMR spectroscopy also confirmed the near complete consumption of the lactide in the crude materials. This demonstrates the efficiency of these catalyst systems and enables accurate control and high loading of both lactide and CO_2 into the resulting triblock copolymers.

The number-average molecular weights (M_n) of the samples were analysed using GPC, in THF and calibrated against narrow M_w polystryrene standards. A value for the calculated M_n was also determined by summing the M_n(GPC) for PCHC and the M_n for the PLA blocks calculated from the conversion of lactide. Generally, the values were in reasonable agreement, however, there were always some discrepancies. The largest discrepancy arises for M_n(GPC) values where the central PCHC block has a lower M_n (entries 5–7), in this case the M_n(GPC) is significantly greater than M_n(Calc). In contrast, using higher M_n PCHC leads to triblock copolymers where the M_n values are lower than the calculated values. Caution must be applied to the values obtained by GPC, as the Mark–Houwink parameters, K and α, are not known for either PCHC or the triblock copolymers. When using the same instrument to estimate the molecular weight of PLA, it has been possible to apply a correction factor (0.58M_n(GPC)).[26] Given the significant discrepancies for shorter PCHC triblocks, it seems that these materials show elution behaviours in GPC more related to PLA, *i.e.* the M_n(GPC) exceed calculated values. This
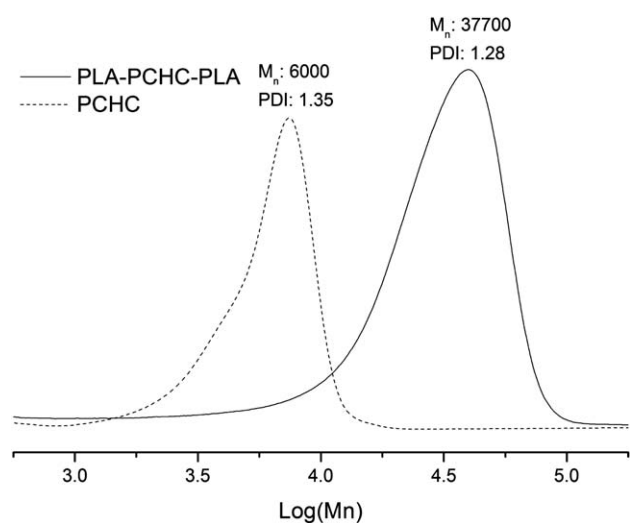

Fig. 3 Expanded overlaid GPC traces of PCHC and PLA-PCHC-PLA (entry 5, Table 1) using THF as an eluent.

is particularly evident on comparing entries 2,5 and 6, where the M_n(GPC), appears to increase on decreasing the molecular weight of the PCHC central block.

The comparison between *S,S*-lactide and *rac*-lactide led to triblock copolymers showing very similar M_n(GPC), ruling out effects of stereochemistry on the M_n. It has already been established that catalyst **3** yields atactic PLA from *rac*-LA and isotactic P(*S,S*)LA from *S,S*-LA.[21a,21b,21d] The triblock copolymer from entry 1, composed of predominantly PLA, was analysed by TGA, which revealed a T_d^{50} of 244 °C. This is consistent with the value for PLA, whilst a small further loss is observed between 270–310 °C, which corresponds to the decomposition of the PCHC block.[17] The glass transition temperatures were measured for all the polymers using differential scanning calorimetry (DSC). All the polymers showed a T_g of approximately 60 °C, corresponding to the lactide portion of the polymer.[27] In some cases, a second, low intensity T_g was observed at 80–95 °C, which corresponds to the T_g of low-weight PCHC (*vide supra*). The observation of two glass transition temperatures is expected for a block-copolymer; that the higher T_g is not always observed is probably due to its low intensity in samples with low loadings of PCHC. In the case of entries 4 and 7, with *S,S*-lactide, a slight

Table 1 Molecular weight (M_n) Data for the PCHC and triblock copoly(LA-CHC-LA)

Entry	M_n PCHC[a] (GPC)/g mol^{-1}	M_n PCHC[b] (NMR) g mol^{-1}	Total lactide eq. (LA stereochem)	M_n[c] (GPC) g mol^{-1}	PDI[c]	M_n[d] (Calc) gmol^{-1}
1	9200	6000	400(*rac*)	51000	1.30	64300
2	9200	6000	200(*rac*)	23500	1.33	36800
3	9200	6000	100(*rac*)	17300	1.34	22500
4	9200	6000	100(*S,S*)	20100	1.38	22600
5	6000	4000	200(*rac*)	37700	1.28	34000
6	2500	2600	200(*rac*)	44900	1.30	29500
7	2500	2600	200(*S,S*)	40800	1.37	30300

[a] Determined using Gel permeation chromatography, with THF as the eluent and calibrated using narrow molecular weight polystyrene standards. [b] Determined from the normalised integrals of H_b and H_c in PCHC ^{1}H NMR spectrum (see Fig. 2). [c] Determined by Gel Permeation Chromatography using THF as eluent and using narrow polystyrene standards. [d] Calculation based upon conversion of lactide to PLA, as calculated from the ^{1}H NMR spectrum of copoly(LA-CHC-LA) and known weight of PCHC block (as determined by GPC).

increase in the T_g of the lactide portion to 65 °C was observed due to the higher crystallinity.

Conclusions

The synthesis of a di-zinc catalyst, with a macrocyclic ancillary ligand and trifluoroacetate co-ligand has been reported. The complex is an efficient catalyst for the copolymerization of cyclohexene oxide and carbon dioxide, under ambient pressures. The poly(cyclohexene carbonate) produced is of low molecular weight (<10 000 g mol^{-1}) and MALDI-ToF analysis shows exclusively hydroxyl end-groups. These arise due to chain transfer or hydrolysis reactions with water. The di-hydroxyl terminated PCHC is used as a macroinitiator in the ring-opening polymerization of lactide, using an active yttrium co-initiator. Near complete conversion of the lactide is achieved yielding ABA-type triblock copolymers. A range of different copolymer block lengths and molecular weights are accessed. The new tri-block copolymers are fully characterised, including an analysis of the molecular weight using GPC and NMR spectroscopy. The block nature of the copolymers is confirmed by DSC experiments which show two glass transition temperatures. The materials are of interest as they represent a high proportion of renewable resource content; thermo-mechanical characterisation of the materials are underway.

Notes and references

1 (a) A. Gandini, *Green Chem.*, 2011, **13**, 1061–1083; (b) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schafer, *Angew. Chem., Int. Ed.*, 2011, **50**, 3854–3871; (c) Y. Xia and R. C. Larock, *Green Chem.*, 2010, **12**, 1893–1909; (d) G. W. Coates and M. A. Hillmyer, *Macromolecules*, 2009, **42**; (e) C. K. Williams and M. A. Hillmyer, *Polym. Rev.*, 2008, **48**, 1–10; (f) A. Gandini, *Macromolecules*, 2008, **41**, 9491–9504; (g) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489; (h) M. S. Lindblad, Y. Liu, A. C. Albertsson, E. Ranucci and S. Karlsson, in *Degradable Aliphatic Polyesters*, Editon edn, 2002, vol. 157, pp. 139–161; (i) R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807.
2 (a) S. Inkinen, M. Hakkarainen, A. C. Albertsson and A. Sodergard, *Biomacromolecules*, 2011, **12**, 523–532; (b) R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835–864; (c) T. P. Wells, J. P. Hallett, C. K. Williams and T. Welton, *J. Org. Chem.*, 2008, **73**, 5585–5588.
3 (a) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11–63; (b) A. P. Dove, *Chem. Commun.*, 2008, 6446–6470; (c) C. K. Williams, *Chem. Soc. Rev.*, 2007, **36**, 1573–1580; (d) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176; (e) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215–2224.
4 (a) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410; (b) H. Sugimoto and S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5561–5573; (c) K. Nozaki, *Pure Appl. Chem.*, 2004, **76**, 541–546; (d) C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405; (e) N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Williams, N. Shah and P. Fennell, *Energy Environ. Sci.*, 2010, **3**, 1645–1669; (f) D. J. Darensbourg, *Inorg. Chem.*, 2010, **49**, 10765–10780; (g) G. A. Luinstra, *Polym. Rev.*, 2008, **48**, 192–219; (h) G. A. Luinstra and F. Molnar, *Macromol. Symp.*, 2007, **259**, 203–209.
5 (a) S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479; (b) K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada and K. Nozaki, *Angew. Chem., Int. Ed.*, 2011, **50**, 4868–4871.
6 S. Inoue, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2861–2871.
7 A. Cyriac, S. H. Lee, J. K. Varghese, E. S. Park, J. H. Park and B. Y. Lee, *Macromolecules*, 2010, **43**, 7398–7401.
8 (a) S. Inoue, H. Koinuma and T. Tsuruta, *J. Polym. Sci., Part B: Polym. Lett.*, 1969, **7**, 287–292; (b) T. Bok, H. Yun and B. Y. Lee, *Inorg. Chem.*, 2006, **45**, 4228–4237; (c) B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S. I. Han, H. S. Yun, H. Lee and Y. W. Park, *J. Am. Chem. Soc.*, 2005, **127**, 3031–3037; (d) W. Kuran and T. Listos, *Makromol. Chem.*, 1992, **193**, 945–956; (e) A. Rokicki and W. J. Kuran, *J. Macromol. Sci.-Rev. Macromol. Chem. Phys.*, 1981, **C21**, 135–186; (f) D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper and J. H. Reibenspies, *J. Am. Chem. Soc.*, 1999, **121**, 107–116; (g) K. L. Orchard, J. E. Harris, A. J. P. White, M. S. P. Shaffer and C. K. Williams, *Organometallics*, 2011, **30**, 2223–2229; (h) K. L. Orchard, A. J. P. White, M. S. P. Shaffer and C. K. Williams, *Organometallics*, 2009, **28**, 5828–5832.
9 (a) S. Inoue, *J. Macromol. Sci., Chem.*, 1979, **13**, 651–664; (b) S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, 2000, **33**, 303–308; (c) C. Chatterjee and M. H. Chisholm, *Inorg. Chem.*, 2011, **50**, 4481–4492; (d) P. Chen, M. H. Chisholm, J. C. Gallucci, X. Zhang and Z. Zhou, *Inorg. Chem.*, 2005, **44**, 2588–2595.
10 (a) K. Nakano, T. Kamada and K. Nozaki, *Angew. Chem., Int. Ed.*, 2006, **45**, 7274–7277; (b) D. J. Darensbourg and R. M. Mackiewicz, *J. Am. Chem. Soc.*, 2005, **127**, 14026–14038; (c) D. J. Darensbourg and A. I. Moncada, *Inorg. Chem.*, 2008, **47**, 10000–10008; (d) D. J. Darensbourg and J. C. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335–6342; (e) B. Li, R. Zhang and X.-B. Lu, *Macromolecules*, 2007, **40**, 2303–2307; (f) X. B. Lu, L. Shi, Y. M. Wang, R. Zhang, Y. J. Zhang, X. J. Peng, Z. C. Zhang and B. Li, *J. Am. Chem. Soc.*, 2006, **128**, 1664–1674; (g) G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt and B. Rieger, *Chem.–Eur. J.*, 2005, **11**, 6298–6314; (h) K. Nakano, S. Hashimoto and K. Nozaki, *Chem. Sci.*, 2010; (i) K. Nakano, M. Nakamura and K. Nozaki, *Macromolecules*, 2009, **42**, 6972–6980; (j) E. K. Noh, S. J. Na, S. Sujith, S. W. Kim and B. Y. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 8082–8083; (k) J. Yoo, S. J. Na, H. C. Park, A. Cyriac and B. Y. Lee, *Dalton Trans.*, 2010, **39**, 2622–2630; (l) C. T. Cohen, C. M. Thomas, K. L. Peretti, E. B. Lobkovsky and G. W. Coates, *Dalton Trans.*, 2006, 237–249; (m) C. T. Cohen and G. W. Coates, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5182–5191; (n) C. T. Cohen, T. Chu and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 10869–10878; (o) Z. Q. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem., Int. Ed.*, 2003, **42**, 5484–5487; (p) S. J. Na, S. S., A. Cyriac, B. E. Kim, J. Yoo, Y. K. Kang, S. J. Han, C. Lee and B. Y. Lee, *Inorg. Chem.*, 2009, **48**, 10455–10465; (q) S. S., J. K. Min, J. E. Seong, S. J. Na and B. Y. Lee, *Angew. Chem., Int. Ed.*, 2008, **47**, 7306–7309; (r) J. E. Seong, S. J. Na, A. Cyriac, B.-W. Kim and B. Y. Lee, *Macromolecules*, 2010, **43**, 903–908.
11 (a) J. E. Seong, S. J. Na, A. Cyriac, B. W. Kim and B. Y. Lee, *Macromolecules*, 2010, **43**, 903–908; (b) D. J. Darensbourg, M. Ulusoy, O. Karroonnirum, R. R. Poland, J. H. Reibenspies and B. Cetinkaya, *Macromolecules*, 2009, **42**, 6992–6998.
12 J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner and G. W. Coates, *Macromolecules*, 2011, **44**, 1110–1113.
13 (a) A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214; (b) M. R. Kember, A. J. P. White and C. K. Williams, *Macromolecules*, 2010, **43**, 2291–2298; (c) M. R. Kember, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2009, **48**, 9535–9542; (d) P. D. Knight, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2008, **47**, 11711–11719; (e) M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem., Int. Ed.*, 2009, **48**, 931–933; (f) M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.
14 (a) Y. Hwang, H. Kim and M. Ree, *Macromol. Symp.*, 2005, **224**, 227–237; (b) Y. T. Hwang, J. W. Jung, M. Ree and H. Kim, *Macromolecules*, 2003, **36**, 8210–8212.
15 S. Q. Liu, J. L. Wang, K. L. Huang, Y. F. Liu and W. K. Wu, *Polym. Bull.*, 2011, **66**, 327–340.
16 K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds/Part B, Applications in coordination,

organometallic, and bioinorganic chemistry 5th edn, Wiley, New York, , 1997.

17 C. Koning, J. Wildeson, R. Parton, B. Plum, P. Steeman and D. J. Darensbourg, *Polymer*, 2001, **42**, 3995–4004.

18 W. J. van Meerendonk, R. Duchateau, C. E. Koning and G.-J. M. Gruter, *Macromolecules*, 2005, **38**, 7306–7313.

19 (*a*) T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 1304–1309; (*b*) C. T. Cohen, T. Chu and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 10869–10878; (*c*) S. J. Na, S. S, A. Cyriac, B. E. Kim, J. Yoo, Y. K. Kang, S. J. Han, C. Lee and B. Y. Lee, *Inorg. Chem.*, 2009, **48**, 10455–10465; (*d*) W.-M. Ren, Z.-W. Liu, Y.-Q. Wen, R. Zhang and X.-B. Lu, *J. Am. Chem. Soc.*, 2009, **131**, 11509–11518.

20 (*a*) A. Cyriac, S. H. Lee and B. Y. Lee, *Polym. Chem.*, 2011, **2**, 950–956; (*b*) USA Pat., 2010; (*c*) WO 2011126195 (A1), 2011; (*d*) WO2010115567, 2010.

21 (*a*) R. H. Platel, A. J. P. White and C. K. Williams, *Chem. Commun.*, 2009, 4115–4117; (*b*) R. H. Platel, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2008, **47**, 6840–6849; (*c*) L. M. Hodgson, R. H. Platel, A. J. P. White and C. K. Williams, *Macromolecules*, 2008, **41**, 8603–8607; (*d*) R. H. Platel, L. M. Hodgson, A. J. P. White and C. K. Williams, *Organometallics*, 2007, **26**, 4955–4963; (*e*) L. M. Hodgson, A. J. P. White and C. K. Williams, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6646–6651; (*f*) R. H. Platel, A. J. P. White and C. K. Williams, *Inorg. Chem.*, 2011, **50**, 7718–7728.

22 Y. L. Xiao, Z. Wang and K. L. Ding, *Chem.–Eur. J.*, 2005, **11**, 3668–3678.

23 H. R. Kricheldorf, S. Rost, C. Wutz and A. Domb, *Macromolecules*, 2005, **38**, 7018–7025.

24 (*a*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176; (*b*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton. Trans.*, 2001.

25 (*a*) A. Haider and C. K. Williams, *C. R. Chim.*, 2011, **14**, 736–744; (*b*) A. F. Haider and C. K. Williams, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2891–2896.

26 A. Kowalski, A. Duda and S. Penczek, *Macromolecules*, 1998, **31**, 2114–2122.

27 A.-C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466–1486.

ART ■ C2PY00543C

Authors Queries

Editor's queries are marked like this... ∎, and for your convenience line numbers are inserted like this... 5

Query Reference	Query	Remarks
1	[INFO-1] Please carefully check the spelling of all author names. This is important for the correct indexing and future citation of your article. No late corrections can be made. FOR YOUR INFORMATION: You can cite this paper before the page numbers are assigned with: (authors), Polym. Chem., DOI: 10.1039/c2py00543c.	
2	Please supply a contents entry and graphical abstract. The image can be in colour, at most 8 cm wide by 4 cm high (a CMYK, 600 dpi TIF file, preferably). The descriptive text should be no longer than 30 words.	
3	Please indicate where Scheme 1 should be cited in the text.	
4	Ref. 1d: Please supply the page numbers	
5	Ref. 10h: Please provide the page numbers	
6	Ref. 20: Please provide more information for the patents such as author, country etc.	
7	Ref. 24b: Please provide the page numbers	

ART ∎ C2PY00543C