18-Membered cyclic esters derived from glycolide and lactide: preparations, structures and coordination to sodium ions†‡

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From reactions between glycolide or lactide (4 equiv.) with 4-dimethylaminopyridine, DMAP (1 equiv.) and $NaBPh_4$ (1 equiv.) in benzene at 70 °C the cyclic ester adducts $(CH_2C(O)O)_6NaBPh_4$ and $(CHMeC(O)O)_6NaBPh_4$ are formed respectively. The structures of the salts $Na[(S,R,S,R,S,R)\text{-}(CH_3CHC(O)O)_6]_2BPh_4\cdot CH_3CN$ and $(CH_2C(O)O)_6NaBPh_4\cdot(CH_3CN)_2$ are reported. The cyclic esters were separated by chromatography and the structures of $(CH_2C(O)O)_6$, $(S,R,R,R,R,R)\text{-}(CHMeC(O)O)_6$ and $(S,S,R,R,R,R)\text{-}(CHMeC(O)O)_6$ were determined. The ^1H and ^{13}C NMR data are reported for one of each of the six enantiomers of $(CHMeC(O)O)_6$ and the two *meso* isomers. The mechanism for the formation of these 18-membered rings is discussed in terms of an initial reaction between DMAP and $NaBPh_4$ in hot benzene that produces NaPh and DMAP : BPh_3 in the presence of the monomer lactide. The cyclic esters $(CHMeC(O)O)_6$ can also be obtained from the reaction between polylactide, PLA, in the presence of DMAP and $NaBPh_4$. The cyclic esters 3-methyl-1,4-dioxane-2,5-dione and 3,6,6-trimethyl-1,4-dioxane-2,5-dione undergo similar ring enlarging reactions to give cyclic 18-membered ring esters as determined by ESI-MS.

Introduction

Ring-opening polymerization, ROP, of cyclic esters such as lactide, LA, and glycolide, G, provides a convenient and useful synthesis of the polyesters: polylactide, PLA, and polyglycolide, PG, both of which find numerous applications as packaging and drug delivery materials.[1] ROP can be brought about by either organic or metal coordinate catalysis and for the latter it is now generally recognized that the propagating species involve metal alkoxide bonds.[2–5] Coordination of the ketonic ester oxygen bond to an electrophilic metal center enhances nucleophilic attack on the ketonic carbon by the adjacent alkoxide oxygen.[2c,6] Consequently, coordinatively unsaturated metal complexes with polar M–OR bonds show the highest activity in ROP.[7] However, as the rates of ROP increase so do the rates of competing side reactions of chain-transfer, trans-esterification and epimerization.[8] The latter reactions are generally not desirable since they lead to loss of stereocontrol and a broadening of the polydispersity of the polymer. Trans-esterification can occur by both inter- and intra-chain reactions, the latter of which leads to cycles. These reactions are collectively shown in Scheme 1.

We recently reported a reaction pathway that led to the formation of cyclic esters derived from LA.[9] This procedure involves a heterogeneous catalyst system wherein a functionalized polystyrene bead, represented as $PSC_6H_4CH_2NH_2$, was allowed to react with an excess of ^{n}BuLi to form a lithiated support $PSC_6H_4CH_2NHLi(LiBu^n)_4$ which in turn was allowed to react with LA. The tethered lithium alkoxide aggregate so formed was reactive to ROP of LA and by intra-chain trans-esterification cycles were reversibly released into the solution. With time the rings so formed constitute a dynamic combinatorial library[10] and it was shown that the introduction of $NaBPh_4$ selectively removed the 18-membered rings from the solution. We describe here a simpler and more general reaction procedure that extends the earlier studies and obviates the need for the use of both ^{n}BuLi and a polystyrene support.

Results and discussion

Synthesis and mechanistic considerations

Hedrick and Waymouth and their coworkers have shown that strong Lewis bases such as DMAP and heterocyclic N-atom stabilized carbenes can act as catalysts for the ROP of LA in solvents such as benzene and CH_2Cl_2 with an initiator alcohol.[3] The proposed mechanism for this reaction involves hydrogen bonding by the alcohol to the ketonic ester oxygen and nucleophilic attack by the Lewis base leading to ring-opening of the LA molecule.[4] The subsequent displacement of the Lewis base by the alkoxide anion leads to the ring-opened product which in turn is an alcohol. This process can then be repeated for the successive enchainments of LA monomers. This led us to consider a similar potential role for the weakly benzene solvated sodium ion when $NaBPh_4$, DMAP and LA are present and the analogy is noted in Scheme 2. The ring opened lactide is now a sodium alkoxide with a positively charged end group. Further ring-opening of LA by the sodium alkoxide may occur and a back-biting intra-chain trans-esterification reaction will lead to cycles with the 18-membered ring cycles being removed from the solution in the form of the less soluble $(CHMeC(O)O)_6NaBPh_4$ complex.

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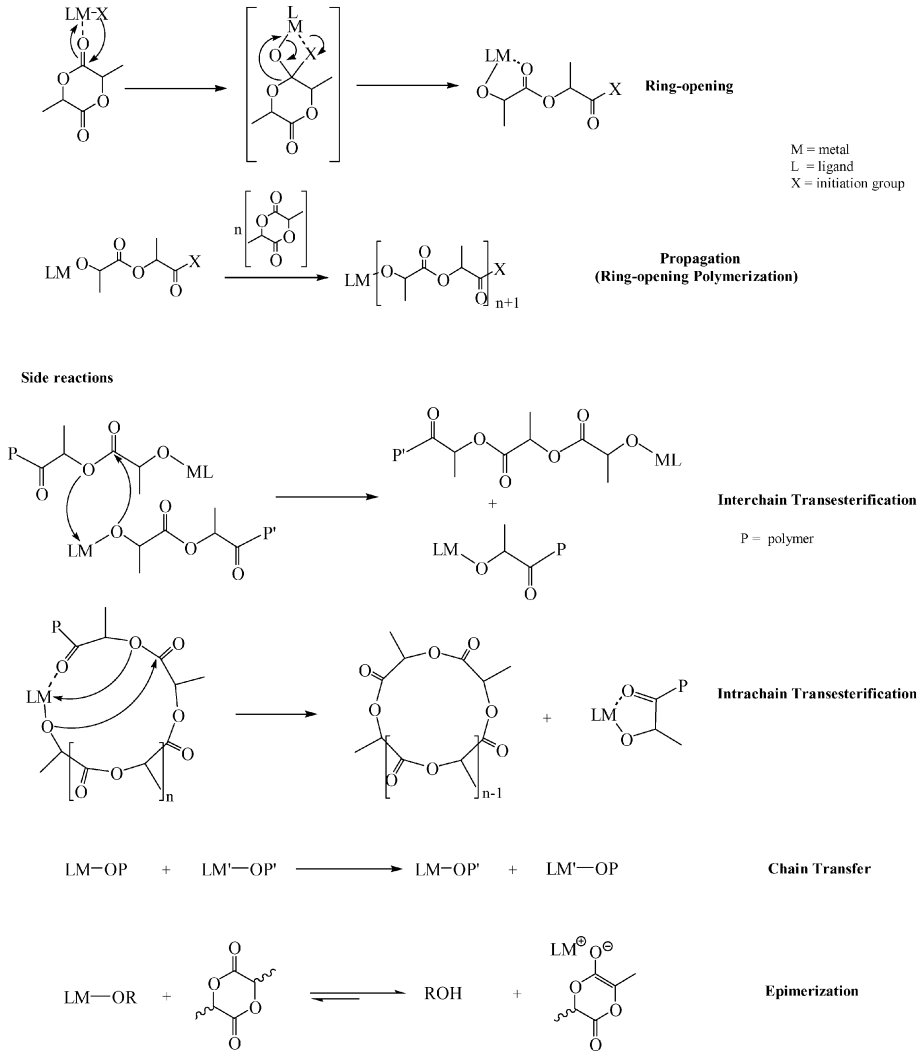
‡ Electronic supplementary information (ESI) available: Listings of bond distances and angles together observed and calculated ^1H NMR spectra for $(CHMeC(O)O)_6$. See DOI: 10.1039/b709081a



Scheme 1 Reactions involved in ring opening polymerization of lactide using a coordination catalyst.

Although the reaction between LA, DMAP and $NaBPh_4$ in benzene at 70 °C gives the 18-membered cyclic esters in *ca.* 80% yield there are a number of reasons to rule out the reaction pathway presented above. First we note that LA and $NaBh_4$ do not react when heated in benzene in the absence of DMAP, nor do DMAP and LA react alone.

We propose that $NaBPh_4$ which is very sparingly soluble in hot benzene reacts reversibly according to eqn (1a):

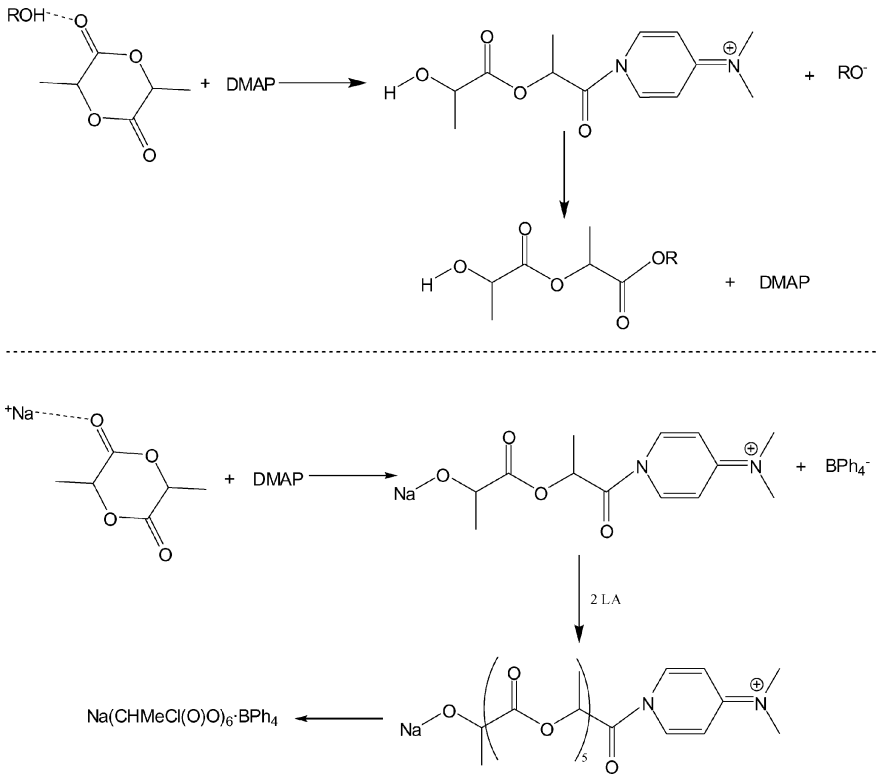
$$NaBPh_4(s) + \text{benzene} \rightleftharpoons Na^+BPh_4^-(\text{benzene}) \quad (1a)$$

$$BPh_4^-(\text{benzene}) + \text{DMAP} \rightleftharpoons Ph^-(\text{benzene}) + \text{DMAP:}BPh_3 \quad (1b)$$

Under normal circumstances reaction (1b) is fully reversible but if there is a reactant present to remove the Ph^- anion, or the solvated Na^+Ph^- ion pair, then reaction (1b) is driven to the right. Thus in the case of wet benzene-d_6, protio benzene is formed (as determined by ^1H NMR spectroscopy). Furthermore, in the presence of LA, ROP is initiated by sodium enolate formation. The formation of benzene is in both instances accompanied by the formation of DMAP:BPh_3 which forms large colorless crystals from benzene solution. The molecular structure of this Lewis base–Lewis acid adduct is shown in Fig. 1. The $NaBPh_4$ thus serves as a sacrificial initiator and as a trap for the cyclic 18-membered esters as they are removed from solution. However, the limited solubility of these products in benzene does mean that, with time and in the presence of an excess of LA, the BPh_4^- ion is slowly converted to DMAP:BPh_3 thus releasing the cyclic esters into solution where they are converted to PLA (or PG in the case of glycolide). This is, indeed, the case as the yield of the cyclic esters decreases with increasing LA (or G) concentration and time of reaction. In the presence of a large excess of LA or G only PLA and PG are obtained at long reaction times.

Complexes with $NaBPh_4$

The cyclic esters sequestered by $NaBPh_4$ were shown by ESI-MS to be predominantly the 18-membered cyclic esters. For the symmetrical monomer molecules LA and G denoted as A_2 and B_2, respectively, these were seen as the sodiated ions A_6Na^+ and B_6Na^+, respectively (see Fig. 2). Smaller amounts of the 21 and 24 membered rings were just detectable as A_7Na^+ or B_7Na^+ and B_8Na^+ ions. For reactions involving the unsymmetric monomers methylglycolide and trimethylglycolide represented as AB and AC



Scheme 2 Proposed active species during chain propagation. Top: DMAP–HOR reaction proposed by Hedrick *et al.*, bottom: DMAP–$NaBPh_4$ proposed by Chisholm *et al.*

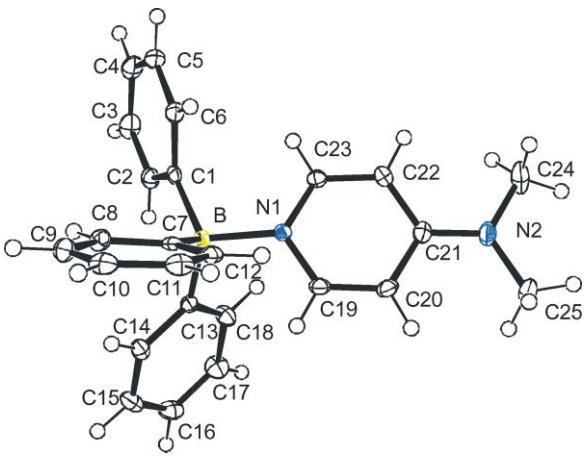


Fig. 1 ORTEP drawing of the structure of DMAP:BPh_3 (**1**) found in solid state.

molecules the 18-membered cyclic esters also predominated. But in addition to the $A_3B_3Na^+$ and $A_3C_3Na^+$ ions, other ions such as $A_2C_4Na^+$, $A_4C_2Na^+$ were clearly present and arise from trans-esterification reactions. These are shown in Fig. 2. In reactions involving equi-molar concentrations of LA (A_2) and G (B_2) the 18-membered $A_nB_mNa^+$ ions indicated that $n < m$ were predominant for $n + m = 6$.

The crude products with $NaBPh_4$ were also examined by ^1H NMR spectroscopy in CD_3CN. In the cases of methylglycolide, AB, the composition of the sequestered esters indicated the presence of the monomers AB, in addition to the A_3B_3 molecules.

$(CH_2C(O)O)_6NaBPh_4\cdot(CH_3CN)_2$ (2). The product of the reaction with glycolide was recrystallized from CH_3CN solution and proved to have the composition of one 18-membered ring, one $NaBPh_4$ and two CH_3CN molecules. By single crystal X-ray crystallography this was shown to have the interesting structure shown in Fig. 3 wherein there is a polymeric chain of Na^+ ions ligated by two different $(CH_2C(O)O)_6$ molecules. One molecule acts as a bridging κ^3,κ^3-ligand wherein three ketonic oxygens are directed to one Na^+ ion in an alternating manner within the ring. The other $(CH_2C(O)O)_6$ molecule is also used as a bridging ligand but only two ketonic oxygens are involved. The Na^+ ions are six-coordinate in a pseudo octahedral environment with two nitrogen atoms from the two CH_3CN molecules completing the coordination sphere.

(*R*,*S*,*R*,*S*,*R*,*S*)-$A_6NaBPh_4CH_3CN$. As noted in the earlier publication dealing with the cyclic esters derived from LA,[9] the 18-membered rings A_6 are formed with epimerization. The *meso* isomer having alternating stereo centers (*R*,*S*,*R*,*S*,*R*,*S*)-A_6 had crystallographically imposed S_6 symmetry and seemed an ideal candidate for forming a polymeric chain with Na^+ ions. In order to test this hypothesis, we separated this *meso* isomer and undertook a reaction with $NaBPh_4$ in acetonitrile. A product of formula $A_6NaBPh_4\cdot CH_3CN$ was indeed obtained as needles and its structure was determined by a single crystal X-ray study. The polymeric chain structure is shown in Fig. 4. The (*R*,*S*,*R*,*S*,*R*,*S*)-A_6 molecule is ideally suited to act as a bridging κ^3,κ^3-O_6 donor, and the O · · · O separation of the nearest ketonic oxygen atoms is 3.53 Å in the free ligand whilst in the complex with $NaBPh_4$ the distance span the range from 3.25 to 3.46 Å.

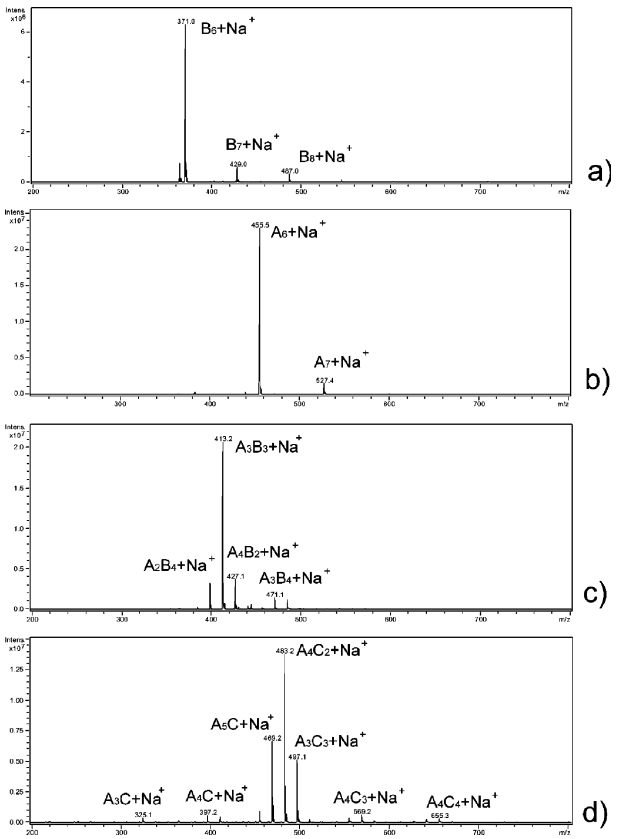


Fig. 2 ESI-MS spectrum for solid part of reactions: (a) $NaBPh_4$ + DMAP + glycolide (B_2); (b) $NaBPh_4$ + DMAP + L-lactide (A_2); (c) $NaBPh_4$ + DMAP + methylglycolide (AB); (d) $NaBPh_4$ + DMAP + trimethylglycolide (AC).

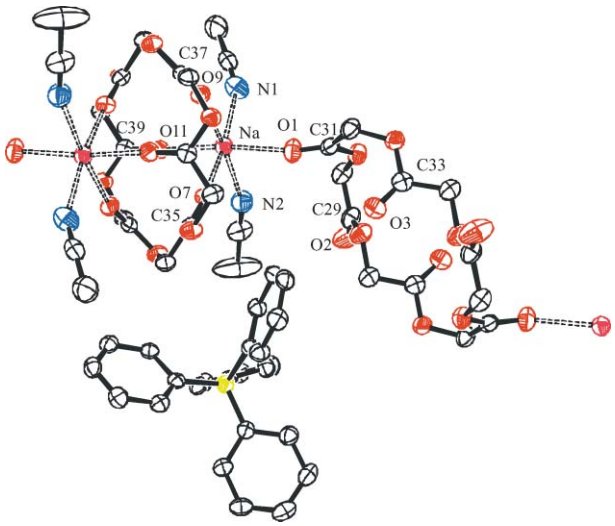


Fig. 3 ORTEP drawing of a section of the polymeric structure of $(CH_2C(O)O)_6Na^+BPh_4^-(CH_3CN)_2$ (**2**) found in the solid state.

The free cyclic esters. Since their preparations employ coordination with Na^+ ions, the challenge to obtain the free esters requires their decomplexation. In order to achieve this we have employed reaction with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, TMEDA, in acetonitrile followed by chromatography with chloroform as eluant. As noted earlier the lactide cyclic esters

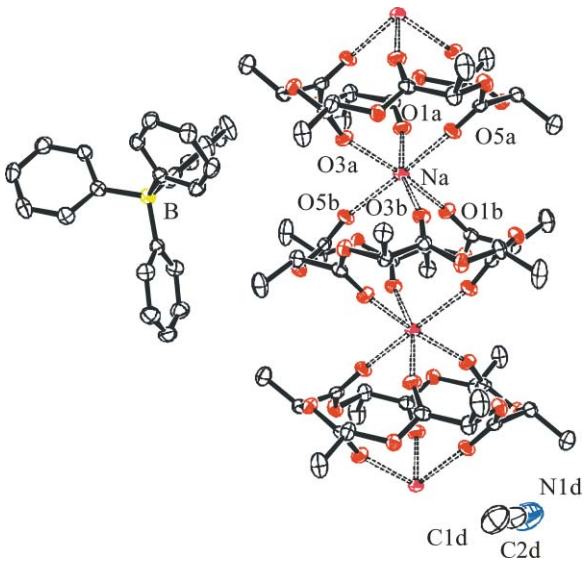


Fig. 4 ORTEP drawing of the molecular structure of $Na[(S,R,S,R,S,R)\text{-}(CH_3CHC(O)O)_6]BPh_4{\cdot}CH_3CN$ (**12**) found in the solid state.

denoted as A_6 are formed with epimerization and thus even though in the initial reaction involving LA the total yield of A_6 is around 80%, the subsequent isolated yield of a specific isomer is much lower. The first isomer to be eluted is the *meso* isomer with the (*S*,*S*,*S*,*R*,*R*,*R*)-stereosequence whose molecular structure was reported previously.[9] The next elute contains three enantiomeric pairs: (*S*,*S*,*R*,*R*,*R*,*R*)/(*R*,*R*,*S*,*S*,*S*,*S*), (*S*,*S*,*R*,*S*,*R*,*R*)/(*R*,*R*,*S*,*R*,*S*,*S*) and (*S*,*R*,*R*,*S*,*R*,*R*)/(*R*,*S*,*S*,*R*,*S*,*S*). The separation of these requires the use of medium pressure liquid chromatography with chloroform as eluant. The structure of the (*S*,*S*,*R*,*R*,*R*,*R*)-$[CHMeC(O)O]_6$ molecule is shown in Fig. 5. Only three of the ketonic oxygen atoms O(3), O(5) and O(7) appear naturally disposed to coordinate with a Na^+ ion.

The next enantiomeric pair to be eluted is (*S*,*R*,*S*,*R*,*R*,*R*)/(*R*,*S*,*R*,*S*,*S*,*S*) followed by (*S*,*R*,*R*,*R*,*R*,*R*)/(*R*,*S*,*S*,*S*,*S*,*S*). Finally (*S*,*S*,*S*,*S*,*S*,*S*)/(*R*,*R*,*R*,*R*,*R*,*R*) and (*R*,*S*,*R*,*S*,*R*,*S*) are eluted with chloroform. At short reaction times when L-LA is used, the 6*S* enantiomer is enriched and with *rac*-LA the 3*S*3*R* and 4*S*2*R*/2*S*4*R* isomers are enriched.

If CH_3CN is used as eluant the $[(S,S,S,S,S,S)\text{-}A_6]_2Na^+$ ion is washed off and can be crystallized as its BPh_4^- salt as described previously. The 6*S*-A_6 molecule is ideally suited to act as a κ^3-O_3 ligand but not as a bridging ligand.

The molecular structure of the (*S*,*R*,*R*,*R*,*R*,*R*)-$(CHMeC(O)O)_6$ molecule formed from D-LA is shown in Fig. 6. The molecule superficially resembles the conformation of the 6*S* isomer seen in the complex ion $(6S\text{-}A_6)_2Na^+$ as the introduction of one different stereocenter, C (11) has only a small influence on the neighboring groups.

The molecular structure of $(CH_2C(O)O)_6$ found in the solid state is shown in Fig. 7. The molecule has a crystallographically imposed center of inversion. In contrast to the (*R*,*S*,*R*,*S*,*R*,*S*)-A_6 molecule which as noted earlier is seemingly predisposed to μ,κ^3,κ^3-coordination, this molecule has only two ketonic oxygen atoms O(1) and O(1)′ pointed inwards and these are on opposite faces of the ring as required by the inversion center. Thus the complexation seen in the solid state structure

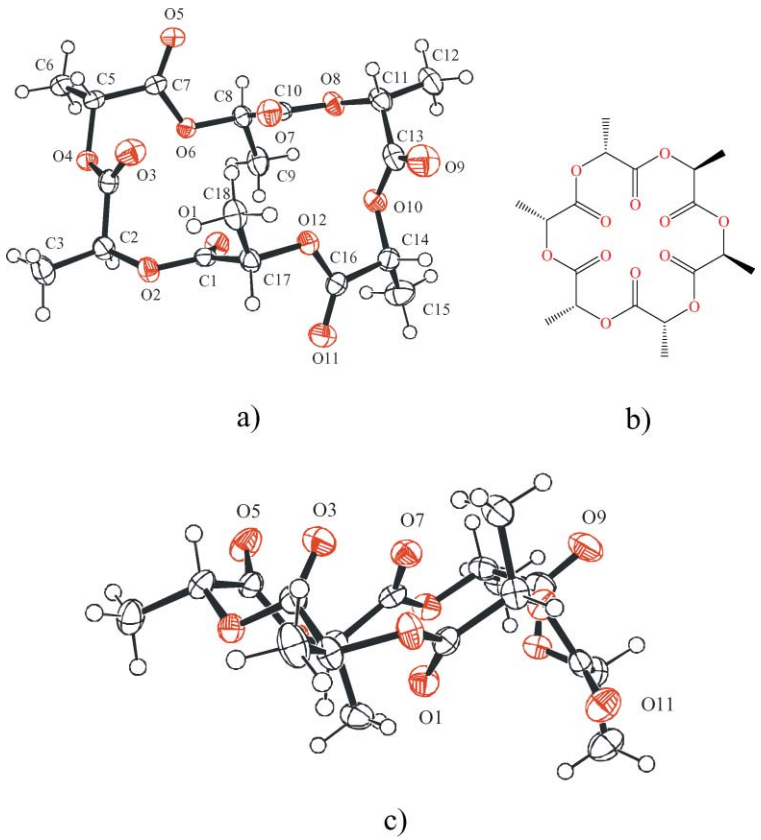


Fig. 5 ORTEP drawing of the molecular structure of (*S*,*S*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**5**) found in the solid state with two views: (a) from top; (c) from side. A line drawing, (b), is also given to show the stereosequence.

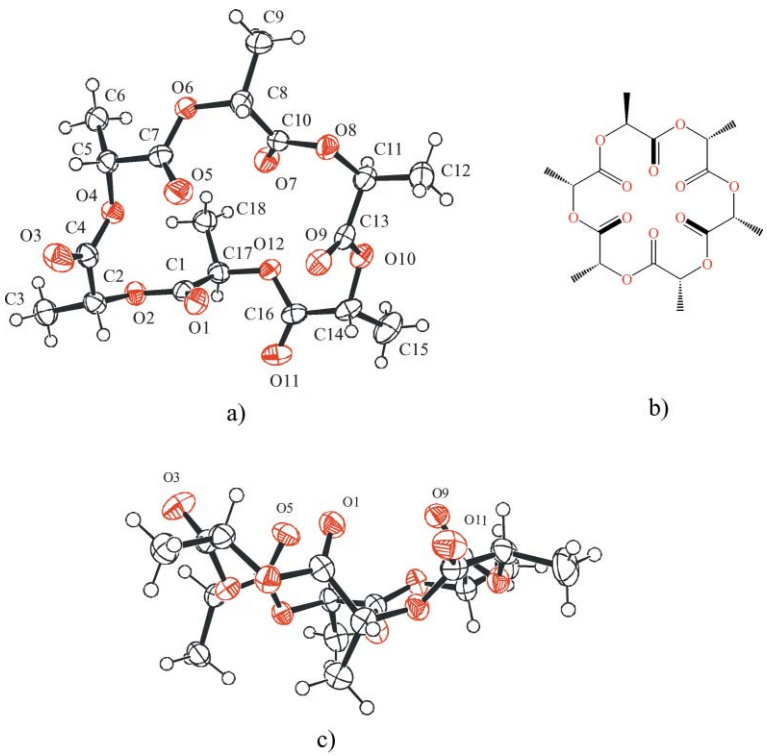


Fig. 6 ORTEP drawing of the molecular structure of (*S*,*R*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**9**) found in the solid state with two views: (a) from top; (c) from side. A line drawing, (b), is also given to show the stereosequence.

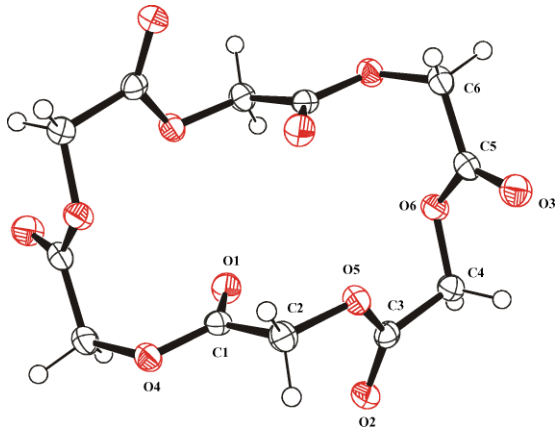


Fig. 7 ORTEP drawing of the structure of $(CH_2C(O)O)_6$ (**3**) found in solid state.

of $(CH_2C(O)O)_6NaBPh_4\cdot(CH_3CN)_2$, which contains two kinds of bridging modes for the cyclic ester, reveals the flexibility of this molecule. The μ,κ^1,κ^1-bridging mode resembles the structure of the free ester and a comparison of the free and coordinated geometries is shown in Fig. 8. The comparison between free (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$ and its corresponding μ,κ^3,κ^3-coordinated 18-membered ring is also shown.

^{1}H NMR spectra of $(CHMeC(O)O)_6$ molecules. As noted earlier the A_6 molecules formed with epimerization give rise to very complex ^{1}H NMR spectra. We have now separated each of the *meso* isomers and the six enantiomeric pairs and consequently can identify each by ^{1}H and $^{13}C\{H\}$ NMR spectroscopy. We have not attempted to separate each enantiomer by chiral chromatography but as noted above reactions employing L-LA give significant enrichment in the 6*S* and 5*S*,*R* enantiomers and likewise D-LA yields 6*R* and 5*R*,*S* which have been structurally characterized.

The 6*S*/6*R* and (*R*,*S*,*R*,*S*,*R*,*S*) molecules exhibit only one methine resonance and one methyl resonance as shown in Fig. 9. The (*S*,*R*,*R*,*S*,*R*,*R*)/(*R*,*S*,*S*,*R*,*S*,*S*) and (*S*,*S*,*S*,*R*,*R*,*R*) molecules which have C_2 and C_i symmetry, respectively, have three methine signals and three methyl signals as shown in Fig. 10. All the other isomers have no element of molecular symmetry and at 500 MHz each give rise to six sets of methine signals which in some instances overlap. These spectra are shown in Fig. 11.

As can be seen from an inspection of Fig. 9, 10 and 11, the methine and methyl proton resonances each span a range of around 0.5 ppm. Given the interest in the assignment of the

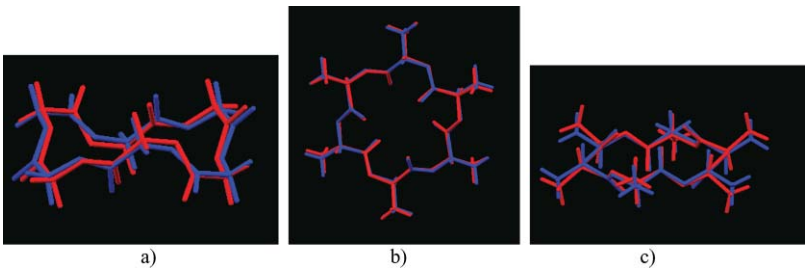


Fig. 8 Stick drawings of 18-membered rings: comparison between free ester and coordinated μ-bridging geometries: (a) $(CH_2C(O)O)_6$ (**3**) (red) and $(CH_2C(O)O)_6NaBPh_4\cdot(CH_3CN)_2$ (**2**) (blue); (b) (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$ (**11**) (blue) and Na[(*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6]_2BPh_4\cdot CH_3CN$ (**12**) (red) from top; (c) side view.

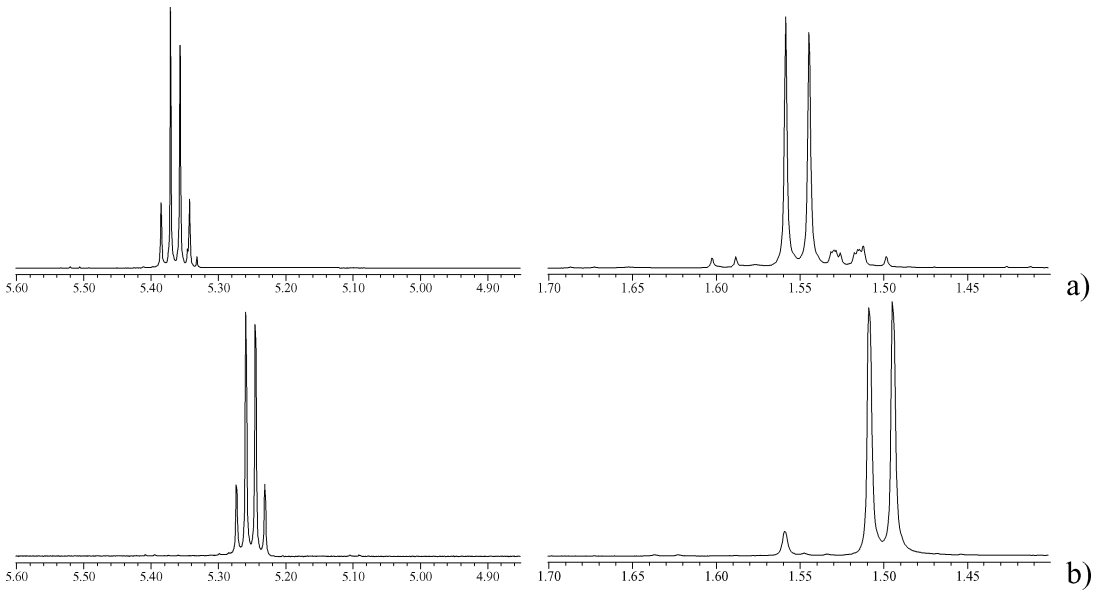


Fig. 9 ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of isomer (a) (*S*,*S*,*S*,*S*,*S*,*S*)- or (*R*,*R*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$, **10**; (b) (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$, **11**.

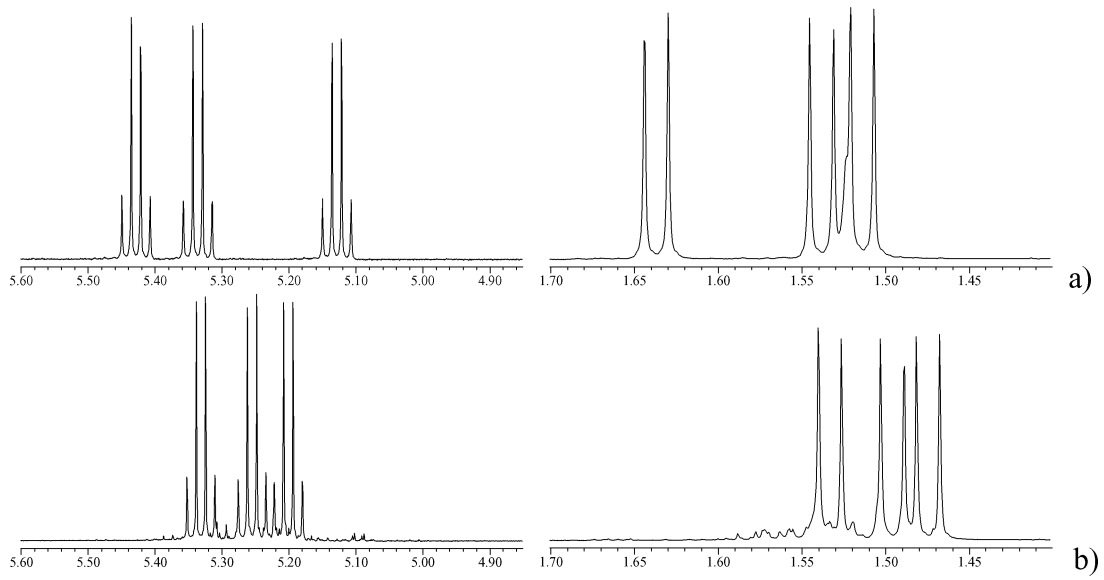


Fig. 10 ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of isomer (a) (*S*,*S*,*S*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$, **4**; (b) (*S*,*R*,*R*,*S*,*R*,*R*)- or (*R*,*S*,*S*,*R*,*S*,*S*)-$(CH_3CHC(O)O)_6$, **7**.

stereosequences of PLA,[11] we were intrigued to know whether modern calculational procedures could be used to make assignments of chemical shifts in these isomers. For the isomers that had been structurally characterized, we took as a starting point the molecular structure found in the solid state and then employed geometry optimization using the Gaussian 03 suite of programs. With the optimized structure, the computed chemical shifts were determined including chloroform as the solvent medium. The calculated chemical shifts are shown along with their respective assignments for the experimental spectra in the electronic supplementary information, ESI.‡ A general conclusion can be stated that the calculated methine resonances are notably more deshielded than those observed by ~0.5 ppm to 1.0 ppm and within a given molecule the calculated trends do not agree well with the observed. However, the predicted trends for the methyl protons were more encouraging but similarly were downfield of the observed. Thus for any given isomer with the exception of the 6*S*(6*R*) and (*R*,*S*,*R*,*S*,*R*,*S*), an absolute assignment is not possible at this time.

Concluding remarks

In the reactions between 1,4-dioxane-2,5-dione and its methylated derivatives with $NaBPh_4$ and DMAP, the $NaBPh_4$ acts as both a sacrificial initiator and as a scavenger in the formation of the 18-membered ring cyclic esters. Based on $NaBPh_4$, the yields of the 18-membered ring cyclic esters fall in the range 50–80%, though the isolation of a given enantiomer or isomer of the lactide-derived products is much less due to the separation procedures. These, however, have not been optimized. Much larger cyclic esters derived from LA have recently been reported from the reactions between *N*-heterocyclic carbenes and LA[12] and these reactions proceed without epimerization and lead to a narrow PDI. Taken together these findings may well herald the development of a new class of materials for molecular transport and delivery.

One further comment on the reaction pathway leading to these cyclic esters seems to be in order. In our earlier work we proposed that the 18-membered rings were removed by $NaBPh_4$ from a dynamic combinatorial library of cyclic esters that were released from a polymer supported catalyst by intra-chain transesterification. The $NaBPh_4$ thus acted as an agent for the chemical amplification of the 18-membered rings. In the present case the reaction path is probably quite different and, as suggested by a reviewer, may represent a novel case of perturbing the Stockmayer[13] equilibria between linear chains and cycles. This is probably quite true since with excess of lactide or glycolide the BPh_4^- ion is completely converted to DMAP:BPh_3 and PLA or PG is obtained. Ito and coworkers[14] showed that in the polymerization of ε-latone by $KOBu^t$ in THF there was a significant concentration of lower molecular weight cycles in addition to chains as predicted by Jacobson and Stockmayer.[13] Clearly in our studies the intimate mechanism remains to be established.

Experimental

General

Standard vacuum line, Schlenk flasks and N_2-atmosphere dry box techniques were employed. Benzene was distilled from a potassium suspension. Acetonitrile and chloroform were distilled from a CaH_2 suspension. Sodium tetraphenylborate was purchased from Aldrich, and used as received. L-, (D,L)-lactide (A_2), glycolide (G_2) were purchased from Aldrich and triply sublimed at 60 °C under 10^{-2} mbar. Poly(L)-lactide (Mn = 5400, PDI 1.05) methylglycolide (AG) and trimethylglycolide (AE) were prepared according to literature procedures.[15,16] ^{1}H and ^{13}C {H} NMR experiments were carried out with a Bruker DPX-400 or 500 spectrometer equipped with a 5 mm broad-band probe. Electro spray ionization mass spectroscopy (ESI-MS) was performed on a Bruker Esquire Ion Trap mass spectrometer (Bremen, Germany) equipped with an orthogonal electrospray source operated in positive ion mode.

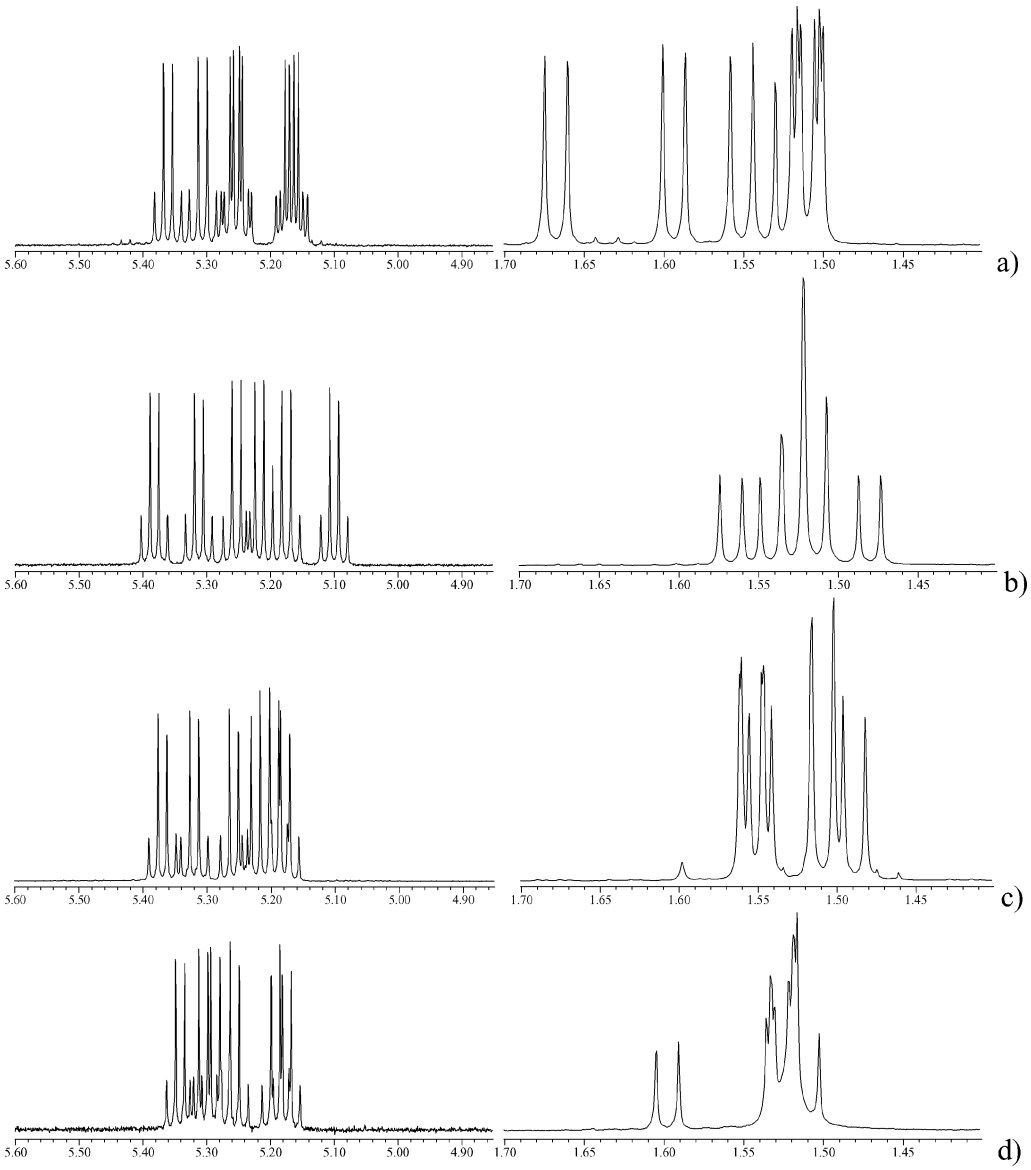


Fig. 11 ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of isomer (a) (*S*,*S*,*R*,*R*,*R*,*R*)- or (*R*,*R*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$, **5**; (b) (*S*,*S*,*R*,*R*,*S*,*R*)- or (*R*,*R*,*S*,*S*,*R*,*S*)-$(CH_3CHC(O)O)_6$, **6**; (c) (*S*,*R*,*S*,*R*,*R*,*R*)- or (*R*,*S*,*R*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$, **8**; (d) (*S*,*R*,*R*,*R*,*R*,*R*)- or (*R*,*S*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$, **9**.

Samples were prepared in a methanol solution and infused into the electrospray source at a rate of 10 μl min^{-1}. Optimal ESI conditions were: capillary voltage 3500 V, source temperature 250 °C, the ESI drying gas was nitrogen. The ion trap was set to pass ions from *m*/*z* 50–2200 amu. Data were acquired in continuum mode until acceptable averaged data were obtained.

X-Ray crystallographic studies

A synchrotron data set for crystal DMAP:BPh_3 (**1**) was collected at the Advanced Photon Source at the beamline ChemMatCARS Sector 15. The work was done at 95 K using a Bruker Smart 6000 diffractometer. The data collection work of $(CH_2C(O)O)_6Na^+BPh_4^-\cdot(CH_3CN)_2$ (**2**), $(CH_2C(O)O)_6$ (**3**), (*S*,*S*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**5**), (*S*,*R*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**9**) and complex Na[(*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6]_2$-$BPh_4\cdot CH_3CN$ (**12**) was done at 150 K, using a Nonius Kappa CCD diffractometer with an Oxford Cryosystems Cryostream Cooler and all the structures were solved by the direct methods procedure in either SHELXS-86 or SHELXS-97.[17] Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97,[18] as incorporated in the WinGX package.[19] The stick-drawings in Fig. 8 were made with the Mercury software package.[20]

Calculations

The calculation was performed with density functional theory and the Gaussian 03 suite of programs.[21] The Cartesian coordinates were obtained from the known A_6 crystal structures. The geometry optimization and vibrational frequency calculations were carried out at the B3LYP/6-311G level. The calculations for NMR chemical shift prediction were performed with the GIAO method and at the B3LYP/6-311G with the PCM method for chloroform.

The standard is the molecule TMS (tetramethylsilane), which was calculated at the same level with the same method.

DMAP and $NaBPh_4$ involved reactions:

1. Preparation of cyclic oligoglycolide, $(CH_2C(O)O)_6$ (**3**). To the mixture of 0.13 g of DMAP (1.1 mmol), 0.17 g of $NaBPh_4$ (0.50 mmol) and 0.37 g of glycolide (3.2 mmol) was added 20 ml of dry C_6H_6, the suspension was stirred at room temperature for 10 h followed by stirring at 70 °C for another 10 h. The resulting mixture was cooled and filtered. The remaining solid was washed with hot C_6H_6 (60 °C, 2 × 10 ml); then 20 ml of CH_3CN was added and the suspension was stirred for 1 h at room temperature before the filtration. The filtrate was transferred into a small vial and slowly evaporated in the air. Crystalline solid was observed at the bottom of the vial when half of the solvent was evaporated. The crystals were isolated from the solution and characterized by ESI-MS, ^{1}H NMR and single crystal X-ray diffraction to have the empirical formula of $(C_2H_2O_2)_6$. Yield: 5.1 mg (1.2%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.80 (s, 12H, CH_2). ^{13}C{H} ($CDCl_3$, 100 MHz): δ 60.90, 166.30. Mp 182–194 °C.

2. Preparation of ligated oligoglycolide, $(CH_2C(O)O)_6$-$Na^+BPh_4^-\cdot(CH_3CN)_2$ (**2**). The solution separated from the crystals above was slowly evaporated to obtain crystalline solid. Yield: 63 mg (18%). $G_6Na^+BPh_4^-(CH_3CN)_2$. ^{1}H NMR(CD_3CN, 400 MHz): δ 4.77 (s, 12H, CH_2), 6.83 (t, 4H, C_6H_5), 6.99 (t, 8H, C_6H_5), 7.27 (m, 8H, C_6H_5). ^{13}C{H} (CD_3CN, 100 MHz): δ 62.17, 122.75, 126.56, 136.72, 167.90.

3. Reaction involving L-LA or PLA as monomer. To the mixture of 0.30 g of DMAP (2.5 mmol), 0.86 g of $NaBPh_4$ (2.5 mmol) and 1.45 g of L-LA or PLA (10.1 mmol) was added 30 ml of dry C_6H_6, and the reaction mixture suspension was then stirred at 70 °C for 10 h. The resulting mixture was cooled and filtered. The remaining solid was washed with hot benzene (60 °C, 2 × 15 ml) and chloroform (2 × 10 ml) before being dried under vacuum, yielding white powder (1.57 g, 81%). ^{1}H NMR and ESI-MS proved that the product has the empirical formula of $(CH_3CHC(O)O)_6NaBPh_4$.

4. Reaction involving methylglycolide as monomer. To the mixture of $NaBPh_4$ (0.20 g, 0.58 mmol), DMAP (0.07 g, 0.65 mmol) and 3-methyl-1,4-dixoane-2,5-dione (methylglycolide, **AB**, 0.37 g, 2.8 mmol) was added 15 ml of benzene and the reaction mixture was stirred at 70 °C for 10 h. The resulting solution was cooled down to r.t. and filtered off. And the remaining solid was washed with hot benzene (60 °C, 2 × 10 ml), chloroform (2 × 5 ml), and dried under vacuum, yielding white solid (0.35 g, 81%). ^{1}H NMR and ESI-MS proved the empirical molecular formula of $[3(AB)\cdot(AB)_3]_{0.5}NaBPh_4$.

5. Reaction involving trimethylglycolide as monomer. To the mixture of $NaBPh_4$ (0.25 g, 0.73 mmol), DMAP (0.08 g, 0.73 mmol) and 3,3,6-trimethyl-1,4-dixoane-2,5-dione [trimethylglycolide, **AC**, 0.50 g, 3.2 mmol) was added 20 ml of benzene and the reaction mixture was stirred at 70 °C for 10 h and then 100 °C for 2 h. Then the solution was cooled down to r.t. and filtered off. The remaining solid was washed with hot benzene (60 °C, 2 × 10 ml), chloroform (2 × 5 ml), and dried under vacuum, yielding a brown solid (0.32 g, 54%). ^{1}H NMR shows the empirical formula of $[AC]_3NaBPh_4$.

6. Reaction involving both L-LA and glycolide as monomer. To the mixture of 0.11 g of DMAP (0.87 mmol), 0.30 g of $NaBPh_4$ (0.87 mmol), 0.30 g of glycolide (G_2, 2.6 mmol), and 0.38 g of L-LA (A_2, 2.6 mmol) was added 20 ml of dry C_6H_6, and the reaction mixture suspension was then stirred at 60 °C for 10 h. The resulting mixture was cooled and filtered. The remaining solid was washed with hot benzene (65 °C, 2 × 15 ml) and chloroform (2 × 10 ml) before being dried under vacuum, yielding a white powder (0.52 g, 81%). ^{1}H NMR and ESI-MS indicated the compositional empirical formula of $(A_{0.8}G_{5.1})NaBPh_4$.

7. Preparation of DMAP-BPh_3 (**1**). To the mixture of $NaBPh_4$ (0.21 g, 0.61 mmol), DMAP (0.10 g, 0.82 mmol) and 3-methyl-1,4-dixoane-2,5-dione (methylglycolide, 0.52 g, 3.4 mmol) was added 15 ml of benzene and the reaction mixture was heated to reflux at 90 °C for 10 h. After the reaction mixture was allowed to stand for 10 d, large and translucent crystals were observed in the solution. The supernatant was then transferred out *via* a cannula, and the crystals were washed with benzene before being dried under vacuum, yielding colorless crystals (80 mg, 36% based on $NaBPh_4$). ^{1}H NMR($CDCl_3$, 400 MHz): δ 8.00 (d, 2H, C_6H_4), 7.19 (m, 15H, C_6H_5), 6.45 (d, 2H, C_6H_4), 3.07 (s, 6H, N-CH_3). Elemental Analysis: Calc: C: 82.35, H: 6.86; Found: C: 82.62, H: 6.99.

Preparation of $(CH_3CHC(O)O)_6$ (A_6) molecules.

1. To the CH_3CN (20 ml) suspension of $[(CH_3CHC(O)O)_6]NaBPh_4$ prepared from *rac*-lactide (2.50 g, 3.38 mmol) was added TMEDA (3.0 ml, 20 mmol) and the reaction mixture was heated to reflux at 90 °C for 20 h. After filtration, the filtrate was evaporated to give a brown sticky solid. The solid was extracted with $CHCl_3$ (15 × 2 ml). The $CHCl_3$ solution was then combined and concentrated and passed through a SiO_2 plug using $CHCl_3$ as eluant to give 1.20 g of waxy solid. The solid was passed through a 1.0 × 15 cm SiO_2 column over $CHCl_3$ at the flow rate of 1 ml min^{-1}, and the collected ingredients were monitored by ^{1}H NMR spectroscopy. The column chromatography gave 2 major ingredients. The column was then washed with CH_3CN and the washing was evaporated under vacuum to give white powder (0.28 g) which was proved to be complex **12**. By applying the LiChroprep™ Si60 MPLC, the first ingredient was separated into 4 components (complex **4**, **5**, **6**, **7**) as shown below. The second ingredient was passed through a SiO_2 column over $CHCl_3$ to give 2 major components (**8** and **9**). The previous solid which was extracted with $CHCl_3$ was treated with TMEDA again under the same condition and worked in the same steps described above to yield the complex **8** and **11**.

(1). (*S*,*S*,*S*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**4**). Yield 35 mg, 2.4%. ^{1}H NMR δ ($CDCl_3$) 5.43 (q, 2H, J = 7.0 Hz, CHMe), 5.34 (q, 2H, J = 7.0 Hz, CHMe), 5.13 (q, 2H, J = 7.0 Hz, CHMe), 1.64 (d, 6H, J = 7.0 Hz, Me), 1.54 (d, 6H, J = 7.0 Hz, Me), 1.51 (d, 6H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 169.39, 169.23, 168.30, (C=O), 69.77, 68.61, 68.34 (CH), 16.84, 16.56, 15.85 (CH_3).

(2). (*S*,*S*,*R*,*R*,*R*,*R*)- or (*R*,*R*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$ (**5**). Yield 10 mg, 0.7%. ^{1}H NMR δ ($CDCl_3$) 5.36 (q, 1H, J = 7.0 Hz, CHMe), 5.31 (q, 1H, J = 7.0 Hz, CHMe), 5.26 (q, 1H, J = 7.0 Hz, CHMe), 5.25 (q, 1H, J = 7.0 Hz, CHMe), 5.17 (q, 1H, J = 7.0 Hz, CHMe), 5.16 (q, 1H, J = 7.0 Hz, CHMe), 1.67 (d, 3H, J = 7.0 Hz, Me), 1.59 (d, 3H, J = 7.0 Hz, Me), 1.55 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 3H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 170.18, 169.61,

169.34, 168.90, 168.48, 167.41 (C=O), 69.79, 69.46, 68.97, 68.83, 68.75, 68.61 (CH), 16.94, 16.64, 16.32, 16.28, 16.21 (CH_3).

(3). (*S*,*S*,*R*,*R*,*S*,*R*)- or (*R*,*R*,*S*,*S*,*R*,*S*)-$(CH_3CHC(O)O)_6$ (**6**). Yield 8 mg, 0.5%. ^{1}H NMR δ ($CDCl_3$) 5.38 (q, 1H, J = 7.0 Hz, CHMe), 5.31 (q, 1H, J = 7.0 Hz, CHMe), 5.25 (q, 1H, J = 7.0 Hz, CHMe), 5.22 (q, 1H, J = 7.0 Hz, CHMe), 5.18 (q, 1H, J = 7.0 Hz, CHMe), 5.10 (q, 1H, J = 7.0 Hz, CHMe), 1.57 (d, 3H, J = 7.0 Hz, Me), 1.54 (d, 3H, J = 7.0 Hz, Me), 1.53 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 6H, J = 7.0 Hz, Me), 1.48 (d, 3H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 169.46, 169.06, 169.03, 168.67 (C=O), 70.00, 69.69, 69.46, 69.42, 68.94, 68.83 (CH), 16.83, 16.73, 16.49, 16.42, 16.35 (CH_3).

(4). (*S*,*R*,*R*,*S*,*R*,*R*)- or (*R*,*S*,*S*,*R*,*S*,*S*)-$(CH_3CHC(O)O)_6$ (**7**). Yield 5 mg, 0.3%. ^{1}H NMR δ ($CDCl_3$) 5.33 (q, 2H, J = 7.0 Hz, CHMe), 5.26 (q, 2H, J = 7.0 Hz, CHMe), 5.20 (q, 2H, J = 7.0 Hz, CHMe), 1.53 (d, 6H, J = 7.0 Hz, Me), 1.50 (d, 6H, J = 7.0 Hz, Me), 1.48 (d, 6H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 169.03, 168.95, 168.84 (C=O), 69.75, 69.51, 68.87 (CH), 16.82, 16.78, 16.31 (CH_3).

(5). (*S*,*R*,*S*,*R*,*R*,*R*)- or (*R*,*S*,*R*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$ (**8**). Yield 0.32 g, 22%. ^{1}H NMR δ ($CDCl_3$) 5.37 (q, 1H, J = 7.0 Hz, CHMe), 5.32 (q, 1H, J = 7.0 Hz, CHMe), 5.26 (q, 1H, J = 7.0 Hz, CHMe), 5.22 (q, 1H, J = 7.0 Hz, CHMe), 5.20 (q, 1H, J = 7.0 Hz, CHMe), 5.18 (q, 1H, J = 7.0 Hz, CHMe), 1.56 (d, 3H, J = 7.0 Hz, Me), 1.55 (d, 3H, J = 7.0 Hz, Me), 1.55 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 6H, J = 7.0 Hz, Me), 1.49 (d, 3H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 169.29, 169.06, 169.04, 168.97, 168.70, 168.28 (C=O), 69.39, 69.16, 69.06, 68.85, 68.71 (CH), 16.67, 16.53, 16.49, 16.41, 16.17 (CH_3).

(6). (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$ (**11**). Yield 54 mg, 3.7%. ^{1}H NMR δ ($CDCl_3$) 5.25 (q, 6H, J = 7.0 Hz, CHMe), 1.50 (d, 18H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 168.97 (C=O), 68.93 (CH), 16.56 (CH_3).

2. Using the $[(CH_3CHC(O)O)_6]NaBPh_4$ prepared from L-lactide (2.01 g, 2.87 mmol) treated with the procedure described in step 1, complex **9**, **10** and **11** were isolated and separated by column chromatography.

(1). (*S*,*R*,*R*,*R*,*R*,*R*)- or (*R*,*S*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$ (**9**). Yield 32 mg, 2.6%. ^{1}H NMR δ ($CDCl_3$) 5.34 (q, 1H, J = 7.0 Hz, CHMe), 5.31 (q, 1H, J = 7.0 Hz, CHMe), 5.29 (q, 1H, J = 7.0 Hz, CHMe), 5.26 (q, 1H, J = 7.0 Hz, CHMe), 5.19 (q, 1H, J = 7.0 Hz, CHMe), 5.17 (q, 1H, J = 7.0 Hz, CHMe), 1.60 (d, 3H, J = 7.0 Hz, Me), 1.53 (d, 3H, J = 7.0 Hz, Me), 1.53 (d, 6H, J = 7.0 Hz, Me), 1.52 (d, 3H, J = 7.0 Hz, Me), 1.51 (d, 3H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 169.60, 169.06, 168.75, 168.56, 168.54, 168.24 (C=O), 69.88, 69.66, 69.37, 69.08 (CH), 16.79, 16.64, 16.59, 16.55, 16.51, 16.45 (CH_3).

(2). (*S*,*S*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$ (**10**). Yield 70 mg, 5.6%. ^{1}H NMR δ ($CDCl_3$) 5.36 (q, 6H, J = 7.0 Hz, CHMe), 1.55 (d, 18H, J = 7.0 Hz, Me); ^{13}C NMR δ ($CDCl_3$) 168.39 (C=O), 69.17 (CH), 16.89 (CH_3).

3. $Na[(S,R,S,R,S,R)\text{-}(CH_3CHC(O)O)_6]BPh_4\cdot CH_3CN$ (**12**). To the mixture of (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$ (25 mg, 0.058 mmol) and $NaBPh_4$ (20 mg, 0.058 mmol) was added 1 ml of C_6H_6 and the reaction mixture was stirred at 90 °C overnight. The reaction suspension was filtered off and the remaining solid was washed with benzene (2 × 3 ml), and dried under vacuum, yielding white solid (32 mg, 71%). The solid was redissolved in CH_3CN and with slow evaporation, crystallographic quality long-needle crystals were obtained. ^{1}H NMR δ (CD_3CN) 7.25 (broad, 8H, CH=C–H), 6.98 (t, 8H, J = 7.2 Hz, CH=C–H), 6.83 (t, 4H, J = 7.2 Hz, CH=C–H), 4.93 (q, 6H, J = 7.0 Hz, CHMe), 1.49 (d, 18H, J = 7.0 Hz, CH_3); ^{13}C NMR δ (CD_3CN) 168.9 (C=O), 128.6, 128.4, 127.9, 127.2 (C_6H_5), 68.8 (CH), 16.9 (CH_3).

Summary of crystal data

DMAP:BPh_3 (**1**): $C_{25}H_{25}BN_2$, M = 364.28, orthorhombic, space group *Pbca*, a = 15.230(1), b = 11.7129(8), c = 22.515(2) Å, V = 4016.4(5) Å^3, T = 95(2) K, Z = 8, μ = 0.015 mm^{-1}, 48843 reflections collected, 3750 independent (R_{int} = 0.054), $R1$ = 0.044 for 3200 reflections with $I > 2\sigma(I)$. $A_6Na^+BPh_4^-(CH_3CN)_2$ (**2**), $C_{40}H_{38}BN_2NaO_{12}$, M = 772.52, triclinic, space group $P\bar{1}$, a = 12.920(1), b = 13.473(1), c = 13.977(2) Å, α = 80.972(4)°, β = 64.021(4)°, γ = 63.137(5)°, V = 1948.6(3) Å^3, T = 150(2) K, Z = 2, μ = 0.106 mm^{-1}, 44653 reflections collected, 6794 independent (R_{int} = 0.045), $R1$ = 0.050 for 4646 reflections with $I > 2\sigma(I)$. A_6-$(CH_2C(O)O)_6$ (**3**). $C_{12}H_{12}O_{12}$, M = 348.22, monoclinic, space group $P2_1/c$, a = 7.668(1), b = 5.901(1), c = 16.004(3) Å, β = 102.408(9)°, V = 707.3(2) Å^3, T = 150(2) K, Z = 2, μ = 0.151 mm^{-1}, 17673 reflections collected, 1618 independent (R_{int} = 0.033), $R1$ = 0.041 for 1313 reflections with $I > 2\sigma(I)$. (*S*,*S*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**5**): $C_{18}H_{24}O_{12}$, M = 432.37, monoclinic, space group $P2_1/n$, a = 8.432(1), b = 16.513(2), c = 14.964(2) Å, β = 93.048(5)°, V = 2080.7(4) Å^3, T = 150(2) K, Z = 4, μ = 0.118 mm^{-1}, 34054 reflections collected, 4751 independent (R_{int} = 0.040), $R1$ = 0.035 for 3455 reflections with $I > 2\sigma(I)$. (*S*,*R*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ (**9**): $C_{18}H_{24}O_{12}$, M = 432.37, orthorhombic, space group $P2_12_12_1$, a = 10.663(2), b = 11.967(3), c = 16.489(4) Å, V = 2104.1(8) Å^3, T = 150(2) K, Z = 4, μ = 0.116 mm^{-1}, 16936 reflections collected, 2124 independent (R_{int} = 0.025), $R1$ = 0.033 for 1925 reflections with $I > 2\sigma(I)$. $Na[(S,R,S,R,S,R)\text{-}(CH_3CHC(O)O)_6]BPh_4\cdot CH_3CN$ (**12**): $C_{44}H_{47}O_{12}NBNa$, M = 815.62, monoclinic, space group $P2_1/n$, a = 9.986(2), b = 19.900(3), c = 21.545(4) Å, β = 90.376(6)°, V = 4281(1) Å^3, T = 150(2) K, Z = 4, μ = 0.100 mm^{-1}, 41693 reflections collected, 7541 independent (R_{int} = 0.052), $R1$ = 0.042 for 4755 reflections with $I > 2\sigma(I)$.

CCDC reference numbers 271310, and 651113–651116.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709081a

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