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Review

Catalytic formation of cyclic-esters and -depsipeptides and chemical amplification by complexation with sodium ions

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Abstract

Lactide, LA, reacts in benzene solution at ~70 °C with a polystyrene supported lithium alkoxide catalyst to release cycles $(CHMeC(O)O)_n$ to the solution by ring-opening polymerization and intra-chain *trans*-esterification. Polylactide, PLA, similarly reacts to yield cycles $(CHMeC(O)O)_n$. The cycles back-react with the supported catalyst and with time form a dynamic combinatorial library of rings from which the 18-membered rings $(CHMeC(O)O)_6$ are selectively removed by complexation with $NaBPh_4$. In this way LA may be converted to $(CHMeC(O)O)_6$ in ~80% yield based on $NaBPh_4$. Similar reactions occur for 3,6-substituted-1,4-dioxane-2,5-diones and 2,5-morpholine diones. These reactions occur with epimerization of the methine carbon stereocenter. In reactions involving 4 equiv. of LA or glycolide and $NaBPh_4$, 4-dimethylaminopyridine in heated benzene the 18-membered cyclic esters form 1:1 adducts with $NaBPh_4$. The structures of several of the isomers of $(CHMeC(O)O)_6$ are reported together with complexes with $NaBPh_4$. The NMR spectra for the two *meso* isomers and the six enantiomers are reported. Similar complexation of $(CH_2C(O)O)_6$, derived from glycolide, to Na^+ is described along with its free unligated structure.

Keywords: Cyclic esters; Alkoxides; Catalysis; Chemical amplification; Lactides; Glycolide

Contents

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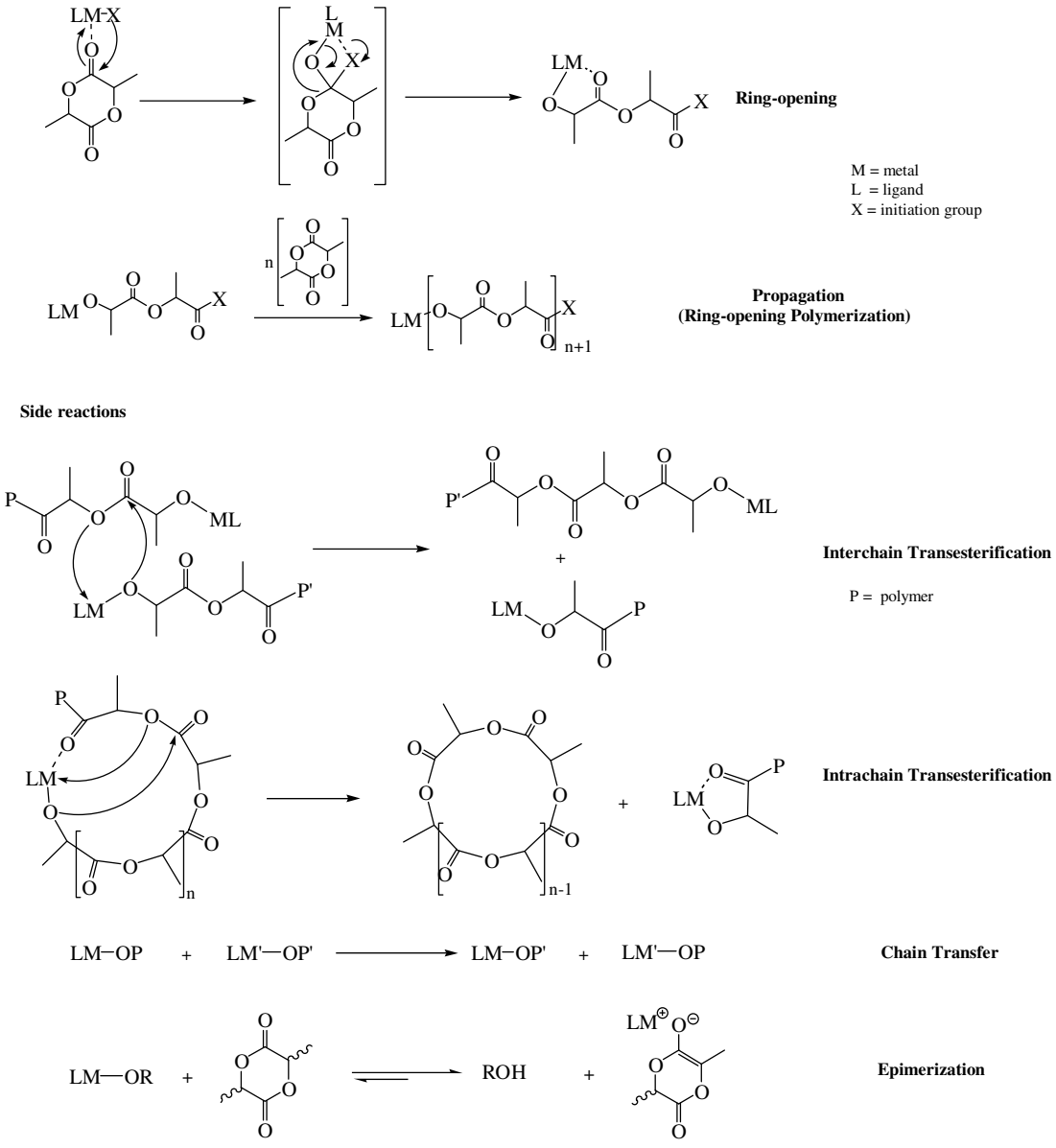
1. Introduction

Ring-opening polymerization of cyclic esters derived from renewable resources such as lactide, LA or glycolide, G yields polyesters, PLA and PG, respectively that find wide ranging applications as specialty products in medicine (sutures, stints, time-release control drugs and tissue polymer matrices), as fibers for clothing and carpeting and as bulk packaging materials. Ring-opening polymerization can be brought about by organic [1–10] and metal-coordinate catalysis [11,12]. The latter has attracted considerable recent attention with respect to stereocontrol in the polymerization of rac-LA and to the development of highly active living catalysts. The reaction pathway leading to polymer formation is shown in Scheme 1. Complexation of the ketonic oxygen of the cyclic ester to an electrophilic metal center activates the ketonic carbon toward nucleophilic attack by a neighboring alkoxide group followed by ring-opening with the reformation of a metal-alkoxide bond. Stereocontrol can arise from chirality of the metal center when the unit LM is chiral and also from the chirality of the M-OCHMe-carbon adjacent to the metal center [13]. Several achiral metal units LM are now known that yield end group stereocontrol in the formation of heterotactic or syndiotactic PLAs [13]. Competing with chain-growth are a number of side reactions and the more active the catalyst the more these side reactions become significant in an undesirable way. Unlike in the polymerization of an olefin which yields a saturated alkane chain, ROP of cyclic esters leads to a polymer that bears the active unsaturated ketonic groups and thus trans-esterification competes with ring-opening. For an active catalyst system,



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

as the monomer concentration decreases and the polymer chains grow this reaction becomes significant and leads to an increase in the polydispersity of the PLA and, in a stereoselective polymerization, to a loss of stereocontrol in the resulting polymer by scrambling the OCHMe centers along the various chains.

Chain transfer can occur by a bimolecular mechanism involving alkoxide bridges, M(μ-OP)(μ-OP′)M′, or by the introduction of an alcohol. The latter may be employed to control the number of growing chains and hence of molecular weight of the polymer because of the reversibility of the reaction shown in Eq. (1) where each added alcohol, ROH initiates the formation of a new living chain POH.

$$L_nM\text{-}OP + ROH \rightleftarrows L_nM\text{-}OR + POH \quad (1)$$

Chain transfer by alkoxide bridge formation has also been shown to bring about stereoselective polymerization by racemic LMOR initiators where chain transfer is more rapid than the ring-opening event [14].

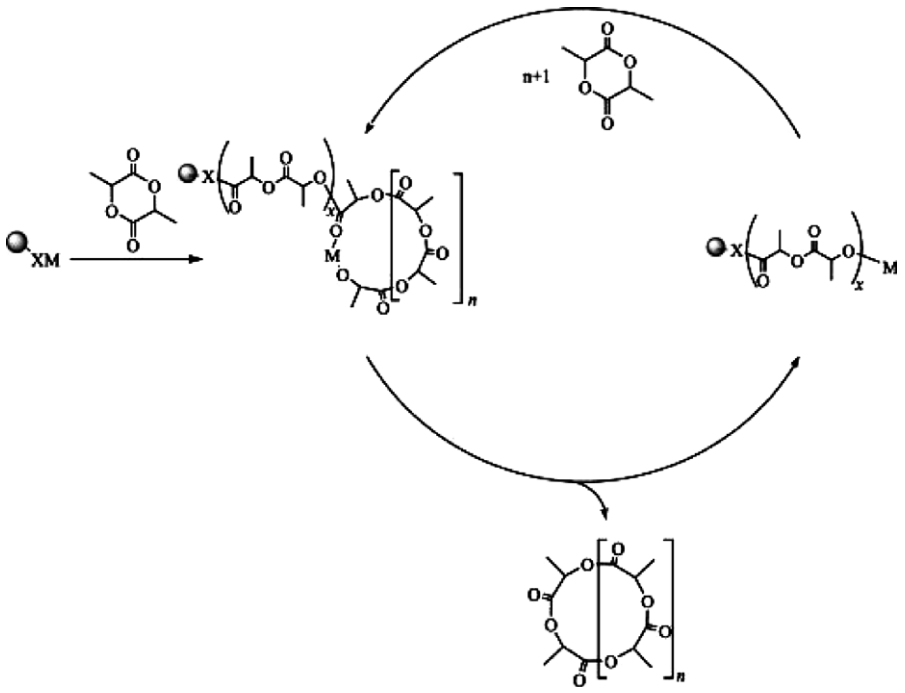
Epimerization of the methine carbon is brought about by alkoxide catalysts of the active group 1 and 2 metals as well as the lanthanide elements. These metal-alkoxide bonds are extremely polar (ionic) and the basicity of the OR group is sufficient to deprotonate the methine carbon to form the enolate, albeit in a reversible manner. Thus polymerization when accompanied by epimerization yields atactic polymers.

As shown in Scheme 1, *trans*-esterification can occur by either an inter-chain or intra-chain process and the latter leads to cycles. We became interested in developing a procedure for the catalytic syntheses of cyclic-oligomers/polymers derived from LA and related ''renewable cyclic esters''. These cyclic oligomers constitute a new class of materials with potential applications for host–guest chemistry and drug delivery. In this article we describe our results in this new venture and note that Waymouth and coworkers have also recently reported the preparation of cyclic esters derived from LA by an organocatalyst procedure involving N-heterocyclic carbenes [15]. Two reports from our lab have previously appeared on this topic [16,17].

2. Results and discussion

2.1. Catalyst preparation and synthesis of cycles

When a commercially available polystyrene support, represented as PS-$C_6H_4CH_2NH_2$, is allowed to react with an excess of $LiBu^n$ in benzene for 72 h the precatalyst PS-$C_6H_4NHLi(LiBu)_x$ where $x \sim 4$ is formed. This is collected by filtration and washed with further aliquots of benzene and dried under vacuum. The formulation given above is based on a Gillman titration [18] that indicates close to 4 equiv. of LiBu with respect to total base. The Li:N ratio of ~5:1 is determined from elemental analysis. It is certainly not unreasonable to formulate this as a polystyrene supported *n*-butyllithium aggregate incorporating a lithium amide group based on the known chemistry of organolithium and amidolithium aggregates. This is then allowed to react with an excess of L-LA in benzene at 60–70 °C and the insoluble polystyrene support is filtered and again washed and dried under vacuum. By elemental analysis the Li to N ratio remains at ~5:1 and we formulate this



Scheme 2. Releasing of cyclic oligolactides from solid supported catalyst. As shown the rings are released containing whole numbers of lactide, but backbiting may occur anywhere along the chains to release rings $(MeCHC(O)O)_n$, where *n* is even or odd.

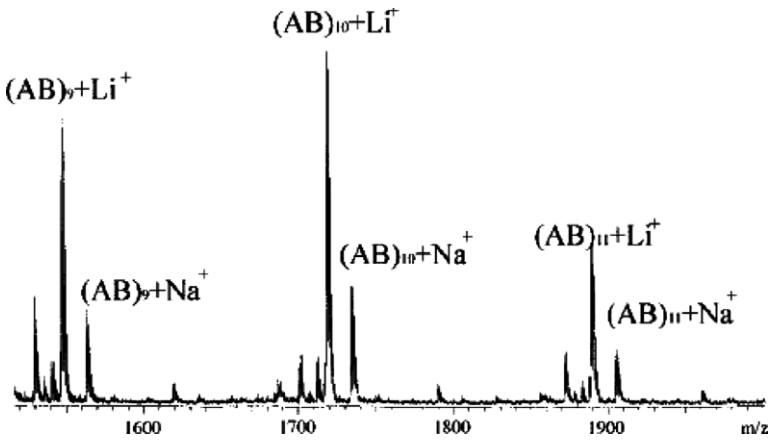


Fig. 1. MALDI-TOF of cyclic 3-isopropyl-6-methyl-2,5-morpholinedione oligomers derived on PS-$C_6H_4CH_2NHLi(BuLi)_x$. AB = $C_8H_{13}O_3N$.

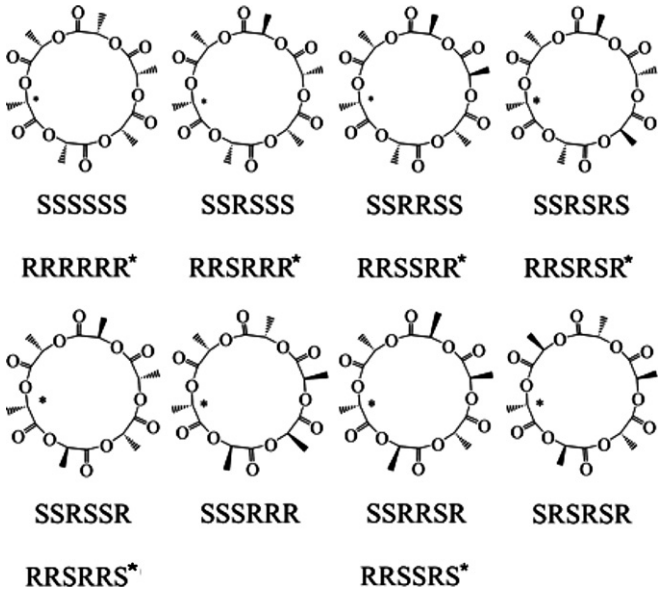


Fig. 2. Stereo isomers of $(CH_3CHC(O)O)_6$ (A_6). Asterisk indicates mirror enantiomer.

as a supported lithium alkoxide cluster where the alkoxide bonds to lithium are formed from ring-opening of the lactide monomers. Analysis of the benzene filtrate by mass spectrometry reveals the presence of LA, oligomers of LA with OH terminal groups and cycles derived from $(LA/2)_n$, where LA/2 = CHMeC(O)O.

The benzene insoluble polymer provides the catalyst for the ring-opening oligomerization of LA and by intra-chain *trans*-esterification cycles are released to the solution. Reactions with LA in benzene at 70 °C over a period of ~10 h present a typical procedure for the formation of rings as represented by Scheme 2. The supported catalyst represented as PS-C_6H_4-$CH_2NH(C(O)CHMeOLi)(LiOR)_4$ is recovered by filtration and dried and is reusable in the same procedure. We have employed this procedure nine consecutive times with little loss of activity. The major loss is a mechanical or physical one involved in the repeated collection of the fine powder. The catalyst system can be viewed as a living or immortal one. Even the presence of small amounts of water can be tolerated since this only releases a small chain but the LiOH/LiOR aggregate remains active in the ring-opening process. As we describe later, the lithium catalyst is also active in epimerization of the methine

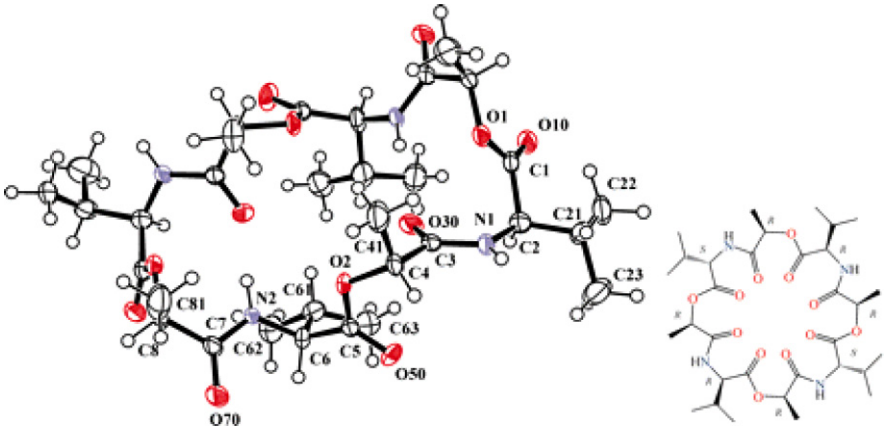
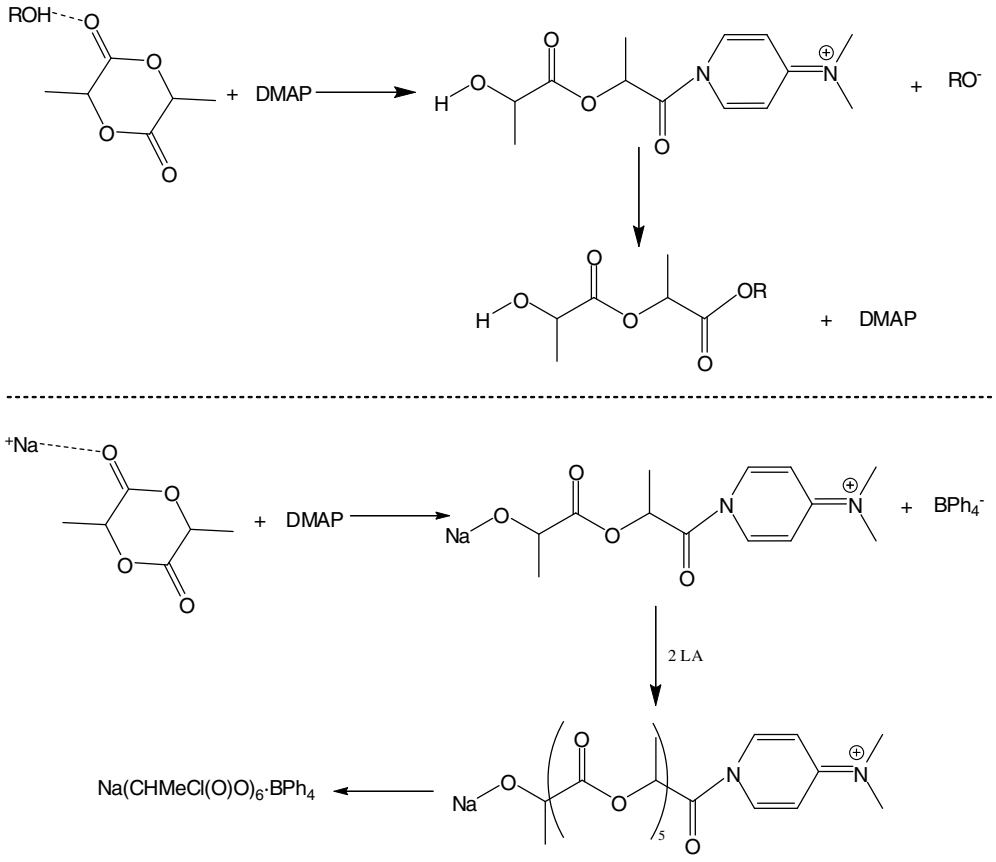


Fig. 3. ORTEP drawing of the molecular structure of cyclic 3-isopropyl-6-methyl-2,5-morphylinedione tetramer found in the solid state. The molecule contains a twofold rotation axis. The ellipsoids are drawn at the 50% probability level. The hydrogen atoms are drawn with an arbitrary radius.



Scheme 3. Proposed active species during chain propagation. Top: DMAP-HOR reaction proposed by Hedrick et al. [1], bottom: DMAP-$NaBPh_4$ proposed by Chisholm et al. [17].

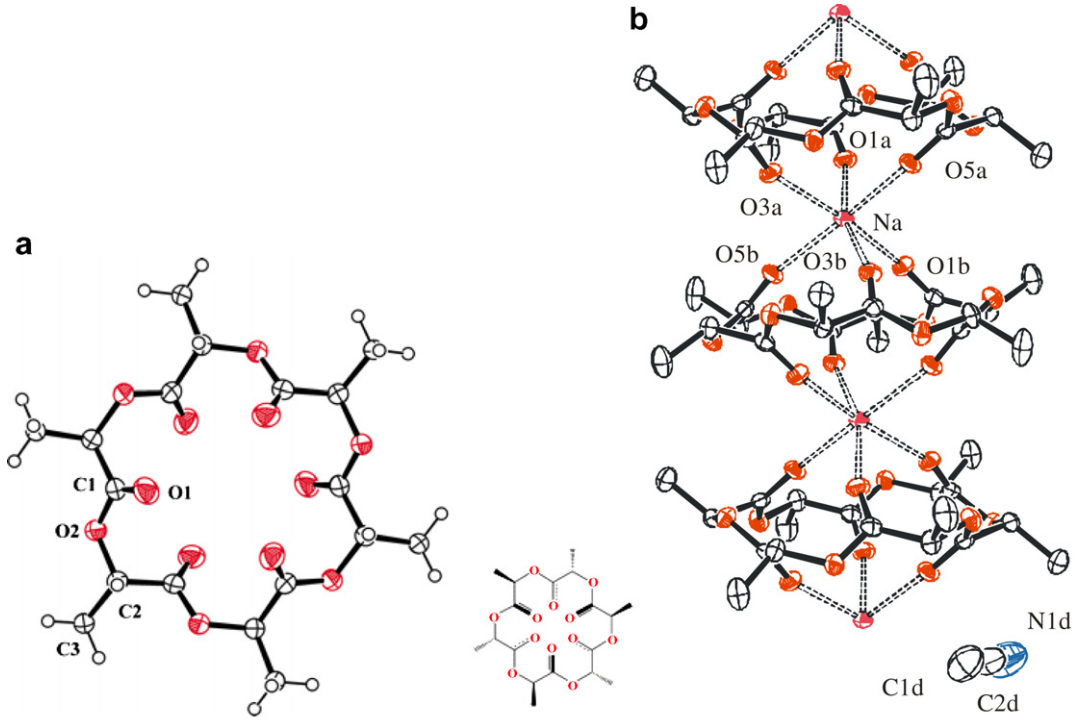


Fig. 4. (a) ORTEP drawing of the molecular structure of (*R*,*S*,*R*,*S*,*R*,*S*)-$(CH(Me)C(O)O)_6$. The ellipsoids are drawn at the 50% probability level and the H atoms are drawn with an arbitrary radius. The molecule has crystallographically imposed S_6 symmetry. (b) A section of the infinite chain of Na^+ ions ligated to the μ,κ^3,κ^3-(*R*,*S*,*R*,*S*,*R*,*S*)-$(CH(Me)C(O)O)_6$ molecules in the solid-state structure of $(CH(Me)C(O)O)_6 \cdot NaBPh_4 \cdot CH_3CN$. The thermal ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity.

carbon. It is also effective in enlarging the rings of other 1,4-dioxane-2,5-diones and 2,5-morpholinediones but not glycolide, *vide infra*. Though glycolide reacts with the support, it is not released as cycles.

2.2. Analyses of the cyclic esters

Mass spectrometry is useful in screening the nature of the products formed in these ring-enlarging reactions. By ESI-MS or MALDI-TOF we observe for lactide a series of sodiated (or lithiated) ions in increasing mass of 72 Da: $A_n \cdot Na^+$, where A = CHMeC(O)O and $n \sim 6$–20. However, for 2,5-morpholinediones which may be represented as AB monomers the ions are of the form $(AB)_n \cdot M^+$ as shown in Fig. 1. Thus in contrast to lactide the ring size increases in multiples of 6, presumably because ring-opening and *trans*-esterification take place preferentially at the ketonic ester group.

In a typical reaction involving ca 10 equiv. of LA per N atom on the support the resulting rings are obtained as a waxy solid with a $M_w \sim 500$–1000 Da and a PDI of ~2.

It is possible to separate some of the smaller rings by GPC but this is a tedious process and as noted earlier the

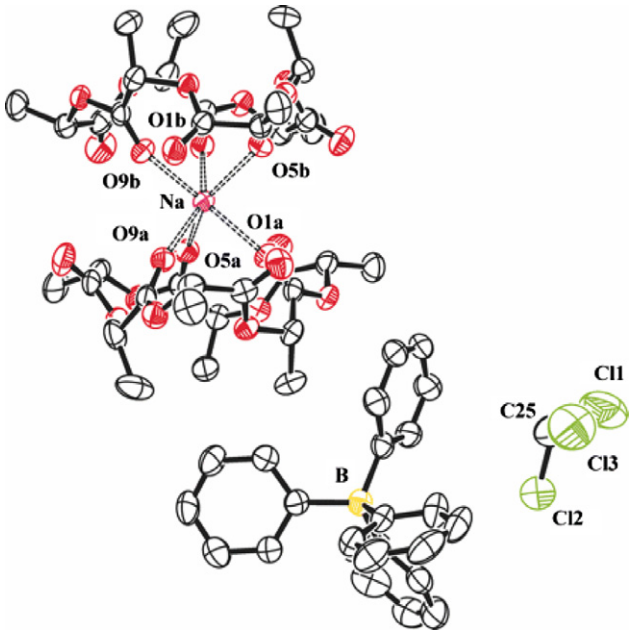


Fig. 6. ORTEP drawing of the molecular structure of $Na[(S,S,S,S,S,S)\text{-}(CH_3CHC(O)O)_6]_2BPh_4 \cdot CHCl_3$ found in the solid state. The ellipsoids are drawn at the 50% probability level. The hydrogen atoms are not shown.

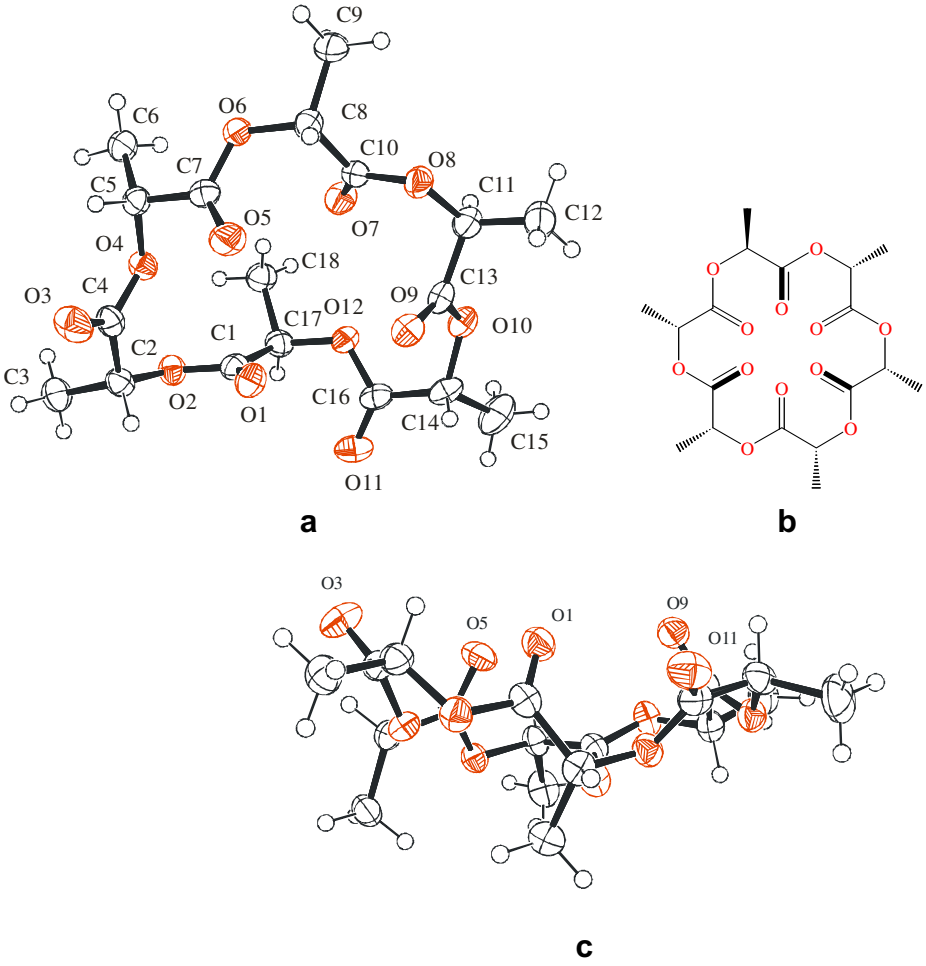


Fig. 5. ORTEP drawing of the molecular structure of $(S,R,R,R,R,R)\text{-}(CH_3CHC(O)O)_6$ found in the solid state with two views: (a) from top; (c) from side. A line drawing, (b) is also given to show the stereo sequence.

rings are formed with epimerization which leads to a large number of enantiomers. For example for the A_6 molecule derived from LA there are two *meso* isomers and six pairs of enantiomers as shown in Fig. 2. This not withstanding specific rings can be obtained by their preferential crystallization in certain solvents. In this manner the *meso* *R*,*S*,*R*,*S*,*R*,*S*-$(CHMeC(O)O)_6$ molecule was first isolated as was the 24-membered cyclodepsipeptide shown in Fig. 3 derived from 3-isopropyl-6-methyl-2,5-morpholinedione. The yield based on monomer in these instances is ca 1–2% which clearly is not a satisfactory synthesis for any specific ring. However, since the rings are themselves cyclic esters they are capable of back-reacting with the supported catalyst and thus with time the rings present in solution will be in equilibrium with each other and LA. They constitute a dynamic combinatorial library [19,20].

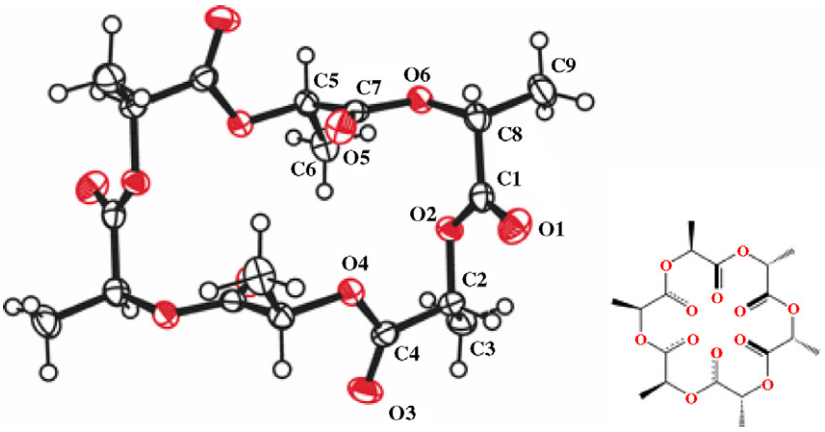


Fig. 7. ORTEP drawing of the molecular structure of (*S*,*S*,*S*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ found in the solid state. The molecule contains a crystallographic inversion center. The ellipsoids are drawn at the 50% probability level. The hydrogen atoms are drawn with an arbitrary radius.

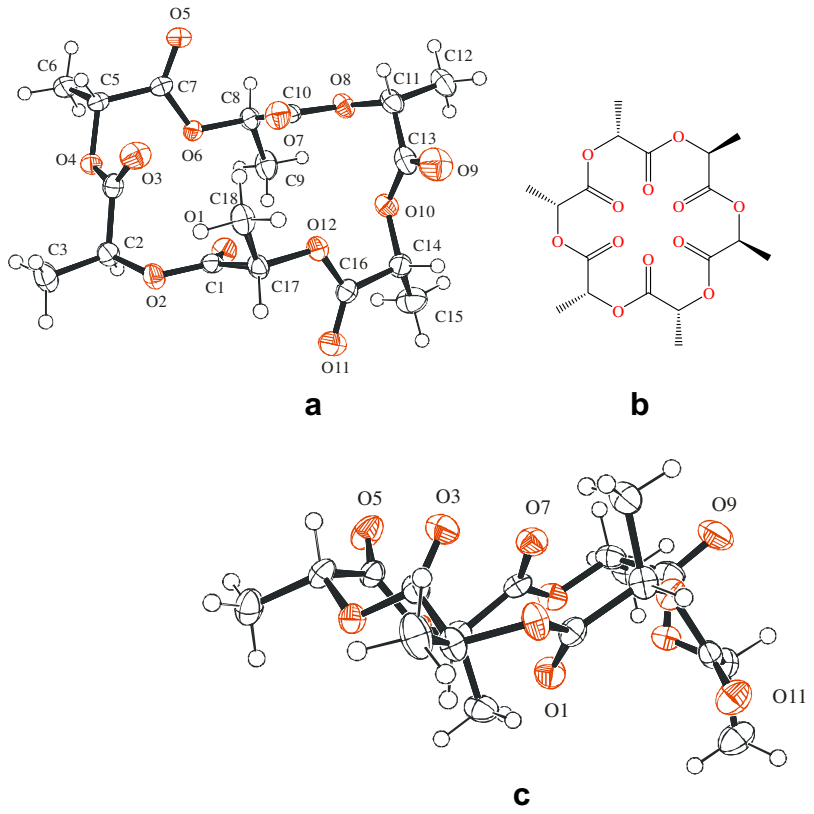


Fig. 8. ORTEP drawing of the molecular structure of (*S*,*S*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$ found in the solid state with two views: (a) from top; (c) from side. A line drawing, (b) is also given to show the stereo sequence. Atoms are drawn at the 50% probability level but H atoms have been assigned an arbitrary radius.

2.3. Chemical amplification of the 18-membered rings

Evidence for a dynamic equilibrium comes from the ability of $NaBPh_4$, which is sparingly soluble in benzene, to sequester the 18-membered rings preferentially and in this manner to act as an agent in their chemical amplification from the mixture of rings. Indeed, in the formation of A_6.$NaBPh_4$ the A_6 rings may be sequestered in ca 80% yield based on LA employed. Similarly if PLA, $M_w \sim 2000$ Da is employed in the reaction with the lithiated supported catalyst in the presence of $NaBPh_4$, the insoluble $A_6 \cdot NaBPh_4$ is formed and can be extracted by dissolving in CH_3CN in which the lithiated catalyst support is insoluble.

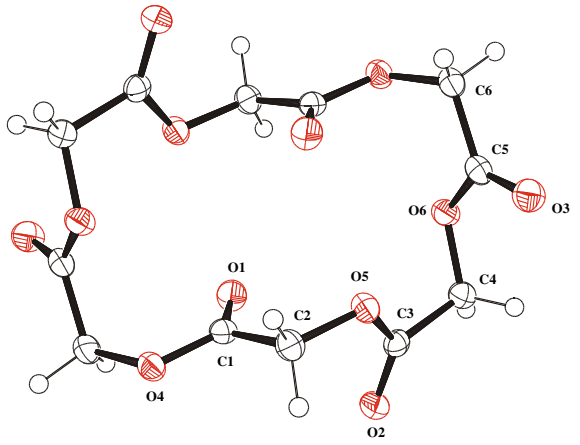


Fig. 9. ORTEP drawing of the structure of $(CH_2C(O)O)_6$ found in solid state. Atoms are drawn at the 50% probability level but H atoms are assigned an arbitrary radius.

2.4. Reactions employing $NaBPh_4$ and 4-dimethylaminopyridine, DMAP

Based on an analogy with the organic catalysis in the ring-opening polymerization of LA by Hedrick and Waymouth [1] employing DMAP and a primary alcohol, we anticipated a similar ring-opening process might occur for the weakly solvated Na^+ ion of $NaBPh_4$ in benzene in the presence of DMAP, see Scheme 3 [17]. This reaction does indeed produce $A_6 \cdot NaBPh_4$ for lactide (LA = A_2) and B_6.$NaBPh_4$ for glycolide (G = B_2) but not by the simple reaction sequence anticipated in Scheme 3. (1) The maximum yield of the sequestered 18-membered ring occurs for a monomer to $NaBPh_4$ to DMAP ratio of 4:1:1. Increasing the monomer ratio decreases the yield of the sequestered rings with the ultimate formation of polymer, either PLA or PG. (2) In all these reactions the 1:1 adduct DMAP:BPh_3 is formed and, in the presence of excess LA, this is the ultimate fate of the BPh_4^- ion. (3) While neither DMAP and LA nor $NaBPh_4$ and LA react in heated benzene there is a reaction when the three components are present.

Our proposal is that DMAP and $NaBPh_4$ react reversibly in heated benzene to form DMAP: BPh_3 and NaPh. In the presence of a substrate, such as LA, that can react with the solvated NaPh, the reaction is driven to the right. $NaBPh_4$ thus acts as both an A_6 scavenger and as a sacrificial initiator in this reaction. If the reaction is carried out in an NMR tube the formation of protio-benzene is readily detected and DMAP:BPh_3 forms large colorless crystals from benzene. Sodium enolates thus act to initiate ROP and by intra-chain *trans*-esterification the A_6.$NaBPh_4$ is removed from solution by its low solubility. With prolonged reaction times and an excess of monomer, however, this reacts further in

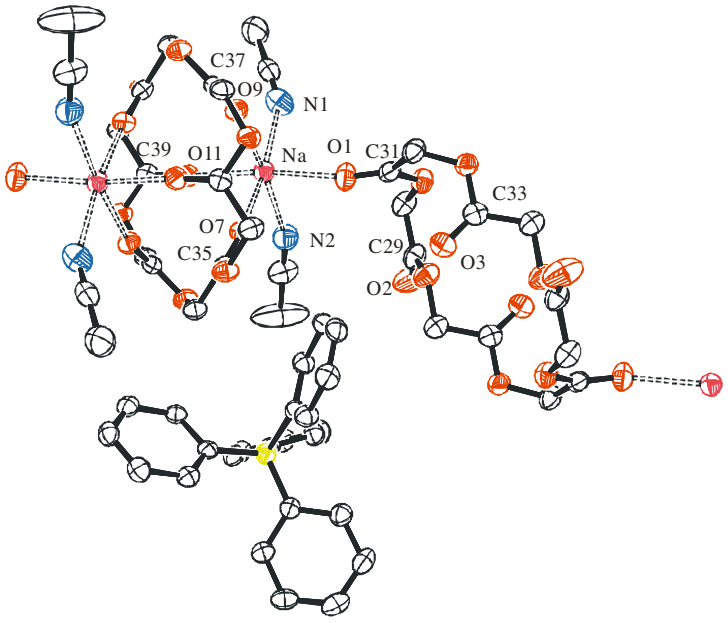


Fig. 10. ORTEP drawing of a section of the polymeric structure of $(CH_2C(O)O)_6Na^+BPh_4^-(CH_3CN)_2$ found in the solid state. Atoms are drawn at 50% probability level and H atoms are omitted for clarity.

the presence of DMAP to give PLA (or in the case of glycolide, PG) and DMAP:BPh_3. The reactions involving L-LA yield epimerized A_6 rings but at short reaction times these are enriched ~50% in the 6*S*-enantiomer with the remainder being in order 5*S*,*R* and 4*S*,2*R*. Conversely, reactions employing rac-LA at short reaction times favor the formation of 4*R*,2*S*/2*R*,4*S* and 3*R*/3*S* isomers.

2.5. Isolation of rings and structural studies

The separation of the 18-membered cyclic esters derived from LA when complexed to $NaBPh_4$ has been achieved by chromatography employing $CHCl_3$ and CH_3CN solvents as eluants. In order to assist in the decomplexation of the Na^+ ion *N*,*N*′-tetramethylethylenediamine, TMEDA, was also employed. Some of the A_6 isomers require the use of medium pressure chromatography to separate them and some are much more difficult to separate from the Na^+ ion because they bind more strongly and require elution with CH_3CN. These matters have been described in detail elsewhere[17] and will not be discussed here further.

The *meso* isomer *R*,*S*,*R*,*S*,*R*,*S*-$(CHMeC(O)O)_6$ crystallizes readily from $CHCl_3$ and in the solid-state has crystallographically imposed S_6 symmetry. Its structure, shown in Fig. 4, can be seen to be naturally disposed to act as a bridging ligand in a μ,κ^3,κ^3-manner having respectively, three ketonic oxygen bonds above and below the ring. Indeed, if this isolated cyclic ester is added to $NaBPh_4$ in CH_3CN in a 1:1 ratio the complex $A_6.NaBPh_4$ is isolated as colorless needles upon crystallization. The solid-state structure of this salt contains an infinite chain of Na^+ ions bridged by μ,κ^3,κ^3-$(CHMeC(O)O)_6$ molecules as was anticipated by

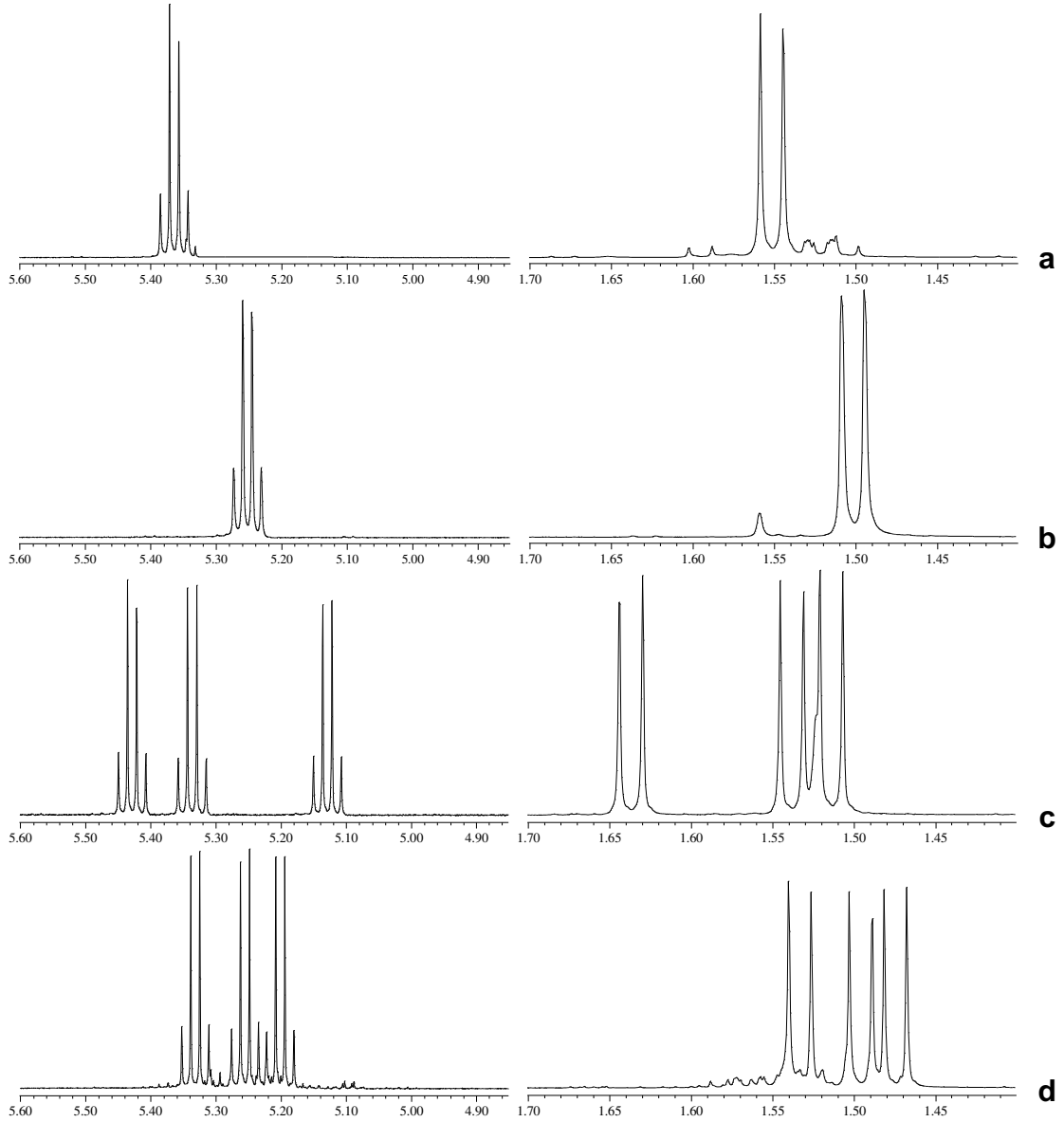


Fig. 11. ^1H NMR spectra ($CDCl_3$, 500 MHz) of isomer (a) (*S*,S,*S*,*S*,*S*,*S*)- or (*R*,*R*,*R*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$, (b) (*S*,*R*,*S*,*R*,*S*,*R*)-$(CH_3CHC(O)O)_6$, (c) (*S*,*S*,*S*,*R*,*R*,*R*)-$(CH_3CHC(O)O)_6$, (d) (*S*,*R*,*R*,*S*,*R*,*R*)- or (*R*,*S*,*S*,*R*,*S*,*S*)-$(CH_3CHC(O)O)_6$.

inspection of the structure of the free ligand, see Fig. 4. In contrast the six *S*-A_6 and six *R* molecules have 3 ketonic oxygens pointing on one side of the 18-membered ring and three pointing outward roughly in the plane of the ring. These enantiomers are best suited in forming 2:1 adducts with the Na^+ ion as is seen in the structure of the salt [*S*,*S*,*S*,*S*,*S*,*S*-$(CHMeC(O)O)_6]_2Na \cdot BPh_4 \cdot CH_3CN$ shown in Fig. 4.

The molecular structure of the native (*S*,*R*,*R*,*R*,*R*,*R*)-A_6 formed from reactions employing D-LA at short reaction times and shown in Fig. 5 superficially resembles the conformation of the 6*S*-A_6 enantiomer seen in the complex ion $(6S\text{-}A_6)_2Na^+$ (Fig. 6) as the introduction of one different stereocenter, C(11) has only a modest influence in the neighboring groups.

Two other structures of native A_6 molecules have been determined. The meso isomer *S*,*S*,*S*,*R*,*R*,*R*-A_6 is shown in Fig. 7 and has C_i molecular symmetry while the *S*,*S*,*R*,*R*,*R*,*R*-A_6 isomer shown in Fig. 8 has no element of symmetry and adopts a chair-like 18-membered ring.

Although in their native structures some A_6 molecules appear more naturally disposed to bind to the Na^+ ion, we anticipate that the two *meso* isomers and each of the six enantiomers are sufficiently flexible to afford efficient binding modes. This seems to be well exemplified for the 18-membered cyclic ester derived from glycolide, $(CH_2C(O)O)_6$ which in its native form shown in Fig. 9 appears not well suited to μ,κ^3,κ^3-bonding to Na^+ yet when recrystallized with $NaBPh_4$ in CH_3CN forms an infinite chain with Na^+ ions

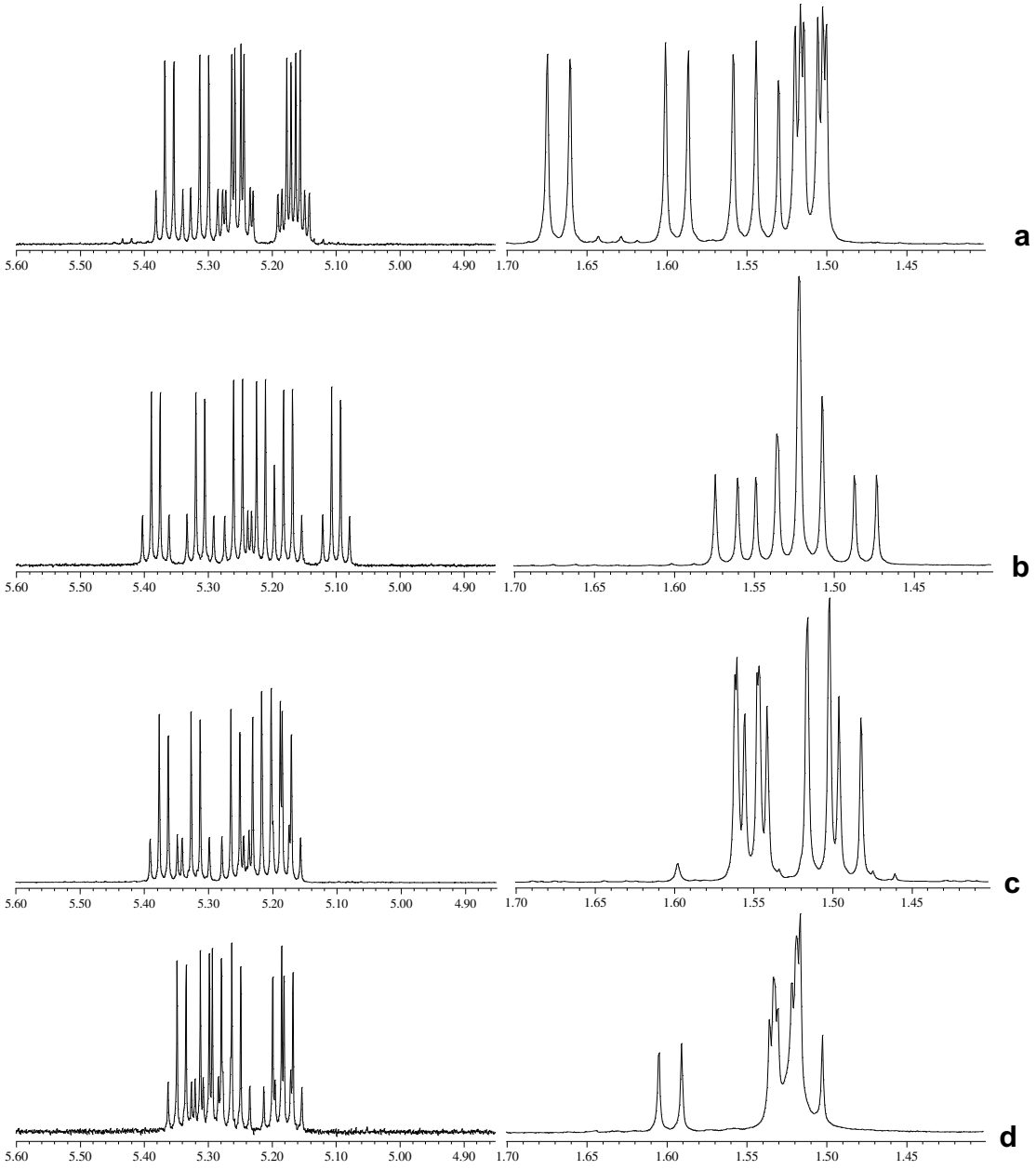


Fig. 12. ^1H NMR spectra ($CDCl_3$, 500 MHz) of isomer (a) (*S*,*S*,*R*,*R*,*R*,*R*)- or (*R*,*R*,*S*,*S*,*S*,*S*)- $(CH_3CHC(O)O)_6$, (b) (*S*,*S*,*R*,*R*,*S*,*R*)- or (*R*,*R*,*S*,*S*,*R*,*S*)-$(CH_3CHC(O)O)_6$, (c) (*S*,*R*,*S*,*R*,*R*,*R*)- or (*R*,*S*,*R*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$, (d) (*S*,*R*,*R*,*R*,*R*,*R*)- or (*R*,*S*,*S*,*S*,*S*,*S*)-$(CH_3CHC(O)O)_6$.

involving μ,κ^1,κ^1 and μ,κ^3,κ^3-bonding modes, see Fig. 10. The μ,κ^1,κ^1 bonding mode resembles closely the structure seen in the solid state for the free ester. No doubt the various A_6 molecules each have a different binding affinity to Na^+ ions but we have not yet evaluated this.

2.6. NMR studies

Analysis of PLAs is generally achieved by an examination of the ^1H or ^{13}C {H} NMR signals of the methine group [13,21,22] and this is very informative in the case of the 18-membered rings $(CHMeC(O)O)_6$. The six *S* and six *R* enantiomers show just a single methine quartet in the ^1H NMR spectrum as does the *meso* (*R*,*S*,*R*,*S*,*R*,*S*) isomer which has S_6 molecular symmetry. The meso isomer *R*,*R*,*R*,*S*,*S*,*S* has a center of inversion and the enantiomers (*S*,*R*,*R*,*S*,*R*,*R*) (*R*,*S*,*S*,*R*,*S*,*S*) have molecular C_2 symmetry and each give rise to three quartets because of the asymmetric nature of linkages –OCH(Me)C(O)–. All other pairs of enantiomers lack any element of symmetry and as such give rise to six methine quartets many of which are partially overlapping at 500 MHz. Representative ^1H NMR spectra are shown in Figs. 11 and 12.

3. Concluding remarks

The procedures described above allow for the conversion of lactide, related cyclic esters (glycolide, methylglycolide, trimethylglycolide) and morpholine-2,5-diones to their respective cyclic oligoesters or cyclodepsipeptides. The enlargement of the rings occurs by the combined operations of ring-opening, monomer enchainment followed by back-biting and ring-expulsion. This and related studies [15] should allow for the development of a new class of materials for transport and release of substrates in molecular assemblies and medicine.

Acknowledgements

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