

# The molecular structure of $(R,S)$ - $[Al_6Bu^t_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$ : evidence for the latent Lewis acid catalyzed polymerization of $(R,S)$ - $\beta$ -butyrolactone

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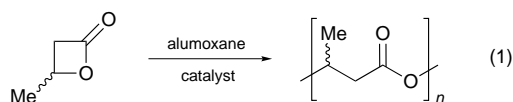
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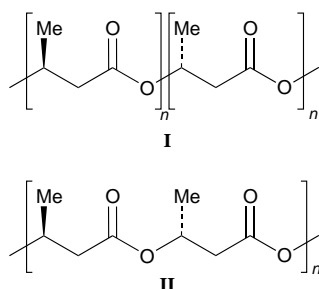
The reaction of  $[Bu^tAl(\mu_3-O)]_6$  with 2 equiv. of  $(R,S)$ - $\beta$ -butyrolactone resulted in the formation of the alumoxane,  $(R,S)$ - $[Al_6Bu^t_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$ , with a molecular structure consisting of two ring-opened lactone moieties inserted into, and bridging, the edge of the  $Al_6O_6$  alumoxane. The role of this alumoxane in the latent Lewis acid catalyzed ring-opening polymerization of  $\beta$ -butyrolactone is discussed.

Alkylalumoxanes,  $(RAIO)_n$ , have been demonstrated to be catalysts for the ring opening polymerization of racemic  $\beta$ -butyrolactone, yielding a crystalline, high molecular mass polymer: poly- $\beta$ -butyrolactone [eqn. (1)].<sup>1</sup>



A range of alumoxane compounds have been investigated for this type of polymerization, including methylalumoxane (MAO), ethylalumoxane (EAO), and isobutylalumoxane (IBAO).<sup>2</sup> The activities of these alumoxane catalysts have been found to be highly dependent on the identity of the alkyl substituent, with the polymerization rates in the following order IBAO > EAO > MAO.

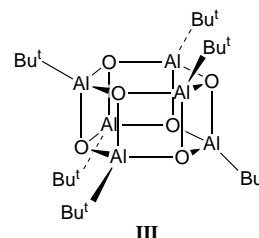
We have recently reported that the individual isolable *tert*-butylalumoxanes,  $[Bu^tAl(\mu_3-O)]_n$  ( $n = 6, 9$ ), are also catalysts, as is a mixture of *tert*-butylalumoxanes (TBAO).<sup>3</sup> However, the stereoregular polymers prepared using MAO, EAO and IBAO are generally found to be isotactic in structure,<sup>4</sup> and it has been proposed that they consist of diads of isotactic sequences of approximately 5–10 repeating units of each configuration of (*R*)- and (*S*)- $\beta$ -hydroxybutyrate unit sequences, **I**.<sup>3</sup> In contrast, the polymers formed using  $[Bu^tAl(\mu_3-O)]_n$  were found to be predominantly syndiotactic in structure **II**.<sup>3</sup>



Irrespective of the details of the polymer microstructure obtained, it is clear that all alumoxane catalysts are able to convert a racemic mixture of  $(R,S)$ - $\beta$ -butyrolactone into a

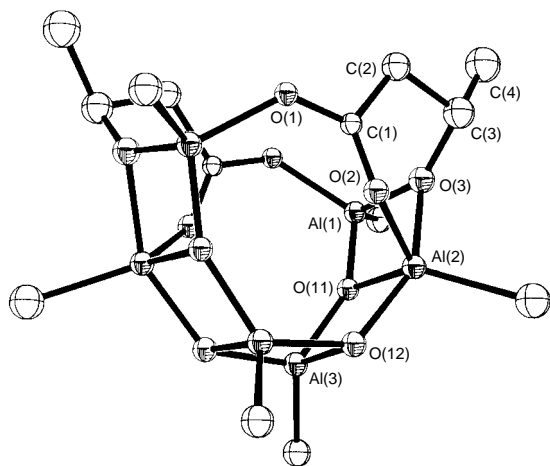
stereoregular polymer by some type of stereospecific or stereoselective propagation step; most likely one involving chain end control. The propagation process is generally agreed to occur by a coordination polymerization mechanism in which the monomer is insertion between the active site on the alumoxane and the growing, covalently bound, polymer chain. However, given the lack of understanding of the structure of alumoxanes in general it is not surprising that the initiation and propagation steps of polymerization are poorly understood.

We have previously demonstrated that the catalytic and co-catalytic activity of the isolable *tert*-butylalumoxanes,  $[Bu^tAl(\mu_3-O)]_n$ , is due to the opening of the  $Al_nO_n$  cage, and we have postulated the term 'latent Lewis acidity' to describe this reactivity.<sup>5</sup> On the basis of these earlier results it is possible that the ring opening polymerization reaction of  $(R,S)$ - $\beta$ -butyrolactone involves the alumoxane cage itself rather than the aluminium alkyl substituents. In that regard, our isolation of individual alkylalumoxanes<sup>6,7</sup> with proven catalytic activity has allowed us to investigate the initiation step in the ring opening polymerization of  $(R,S)$ - $\beta$ -butyrolactone and we report herein the product formed from the reaction of hexameric alumoxane,  $[Bu^tAl(\mu_3-O)]_6$  **III** with this monomer.



Addition of 2 equiv. of  $(R,S)$ - $\beta$ -butyrolactone to a hexane solution of  $[Bu^tAl(\mu_3-O)]_6$  at 25 °C, resulted in the formation of crystalline  $(R,S)$ - $[Al_6Bu^t_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$  in ca. 30% yield. Use of only 1 equiv. of  $(R,S)$ - $\beta$ -butyrolactone gave a lower yield of the same product. Although stable as a solid,  $(R,S)$ - $[Al_6Bu^t_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$  decomposes in solution at room temp., producing unidentified products. However, X-ray quality crystals were obtained from the reaction mixture under suitable conditions. For example, reaction of  $[Bu^tAl(\mu_3-O)]_6$  (650 mg) in hexane (25 cm<sup>3</sup>) mixed with  $(R,S)$ - $\beta$ -butyrolactone (0.18 cm<sup>3</sup>) and allowed to stand, undisturbed, for 24 h.

The molecular structure of  $(R,S)$ - $[Al_6Bu^t_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$ , which resides on a crystallographic twofold axis, was determined by X-ray crystallography and is shown in Fig. 1.† The core structure consists of an  $Al_6O_4$  ladder in a curved conformation, bridged by two  $[O_2CCH_2C(H)(Me)O]$  ligands. The structure may be described as being derived from the opening of two adjacent edges of the hexagonal prismatic core of  $[Bu^tAl(\mu_3-O)]_6$  and insertion of two



**Fig. 1** Molecular structure of  $(R,S)$ - $[Al_6Bu_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$ . Thermal ellipsoids are shown at the 30% level. All hydrogen atoms and *tert*-butyl methyl groups are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Al(1)–O(1a) 1.82(1), Al(1)–O(3) 1.77(1), Al(1)–O(11) 1.71(1), Al(2)–O(2) 1.887(9), Al(2)–O(3) 1.99(1), Al(2)–O(11) 1.91(1); Al(2)–O(12) 1.807(9), Al(3)–O(11) 1.800(9), Al(3)–O(12) 1.84(1), Al(3)–O(12a) 1.79(1), C(1)–O(1) 1.29(1), C(1)–O(2) 1.23(1); O(1a)–Al(1)–O(3) 104.1(5), O(1a)–Al(1)–O(11) 108.6(5), O(3)–Al(1)–O(11) 85.9(5), O(2)–Al(2)–O(3) 85.4(4), O(2)–Al(2)–O(11) 118.2(4), O(2)–Al(2)–O(12) 89.1(4), O(3)–Al(2)–O(11) 75.0(4), O(3)–Al(2)–O(12) 152.1(5), O(11)–Al(2)–O(12) 83.7(4), O(11)–Al(3)–O(12) 85.7(4), O(11)–Al(3)–O(12a) 122.0(4), O(12)–Al(3)–O(12a) 86.7(4), Al(1a)–O(1)–C(1) 131.1(8), Al(2)–O(2)–C(1) 131.8(8), Al(1)–O(3)–Al(2) 96.8(5), Al(1)–O(3)–C(3) 138(1), Al(2)–O(3)–C(3) 119(1), Al(1)–O(11)–Al(2) 102.1(5), Al(1)–O(11)–Al(3) 155.1(5), Al(2)–O(11)–Al(3) 94.2(5), Al(2)–O(12)–Al(3) 96.2(5), O(1)–C(1)–O(2) 122(1).

molecules of  $\beta$ -hydroxybutyrate between the sides of the ladder. In this regard the cage opened core of  $(R,S)$ - $[Al_6Bu_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$  is unlike our previously characterized products from the latent Lewis acid reactions of  $[Bu^tAl(\mu_3-O)]_6$  in which opposite edges are ordinarily opened.<sup>5</sup>

The geometries and bond distances around the Al and O atoms<sup>†</sup> are similar to those we have previously reported for other *tert*-butyl alumoxane compounds.<sup>6,7</sup> One unusual feature of the structure, however, is the presence of the two five-coordinate aluminium centers, Al(2) and Al(2a). As is common for five-coordinate aluminium, the geometry about Al(2) is that of a distorted trigonal bipyramid; O(3)–Al(2)–O(12) 152.1(5) $^\circ$ , and  $\Sigma(X_{eq}-Al-X_{eq}) = 359.3(6)^\circ$ . The  $[O_2CCH_2C(H)(Me)O]$ -ligands, formed from the ring opening of the  $\beta$ -butyrolactone, each cap three of the aluminium atoms. The carboxylate moiety bridges atoms Al(1a) and Al(2), while the alkoxide terminus bridges atoms Al(1) and Al(2). The bond lengths and angles within the carboxylate unit are typical of such moieties<sup>8</sup> and are indicative of delocalization within the carboxylate group. The O–C–O angle [122(1) $^\circ$ ] is similar to that in 'free' carboxylic acids. The carboxylate bite distance [Al(1a)–Al(2) 4.78 Å] is, however, significantly longer than previously observed for aluminium carboxylates (3.26–4.18 Å).<sup>8</sup> Unlike other types of bridging alkoxide compounds the Al( $\mu$ -OR)Al unit is asymmetrical, presumably due to the presence of both four- and five-

coordinate aluminium centers and/or the ring strain within the cage.

Based on the structure described above, we can conclude that the ring-opening reaction of a  $\beta$ -butyrolactone by an alumoxane occurs by attack on the lactone's carbonyl group by the basic alumoxane oxo-ligands rather than by the alumoxane's alkyl substituents. This proposal is in line with our previous results which have shown that while the alkyl groups are relatively inert, the oxide ligands are basic, *e.g.*, they are readily protonated by even relatively weak acids.<sup>9</sup> Thus, it is clear from the structure of  $(R,S)$ - $[Al_6Bu_6(\mu_3-O)_4\{\mu_3-O_2CCH_2C(H)(Me)O\}_2]$ , and its activity as a polymerization catalyst, that the latent Lewis acid mechanism previously proposed for the ring opening of propylene oxide<sup>10</sup> is most likely involved in the initiation step in the polymerization of  $\beta$ -butyrolactone by *tert*-butylaluminum. In addition, similar derivatives may be involved in the polymerization reactions of this monomer with other alkylaluminum.

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## Footnotes and References

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† Crystal data for  $C_{32}H_{66}Al_6O_{10}$ ,  $M = 772.77$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 25.819(2)$ ,  $b = 10.5579(9)$ ,  $c = 18.902(1)$  Å,  $\beta = 118.030(7)^\circ$ ,  $U = 4548.2(7)$  Å<sup>3</sup>,  $D_c = 1.128$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 1664$ , Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\mu = 1.80$  cm<sup>-1</sup>, Enraf-Nonius CAD-4 automated diffractometer, 3033 reflections collected,  $2\theta \leq 44^\circ$ , absorption (DIFABS) correction, 2967 unique reflections and 756 having with  $F > 6\sigma(F)$ . Structure solved by direct methods (SHELXS-86), and Fourier difference synthesis. Refinement by full-matrix least squares with all non-hydrogen atoms isotropic. Hydrogen atoms were placed in calculated positions [ $d(C-H) = 0.95$  Å,  $U(H) = 1.2 U_{eq}$  (attached carbon)], converged  $R = 0.0567$ ,  $R_w = 0.0794$ . CCDC 182/624.

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