

DFT computational details

All calculations were performed using the Gaussian09 suite of codes (revision D.01).¹ Geometries were fully optimised without any symmetry or geometry constraints. The nature of all the stationary points as minima was verified by calculations of the vibrational frequency spectrum, and characterised by no imaginary mode. Only the intermediates of lowest free enthalpy found are reported here. Free enthalpies were calculated within the harmonic approximation for vibrational frequencies.

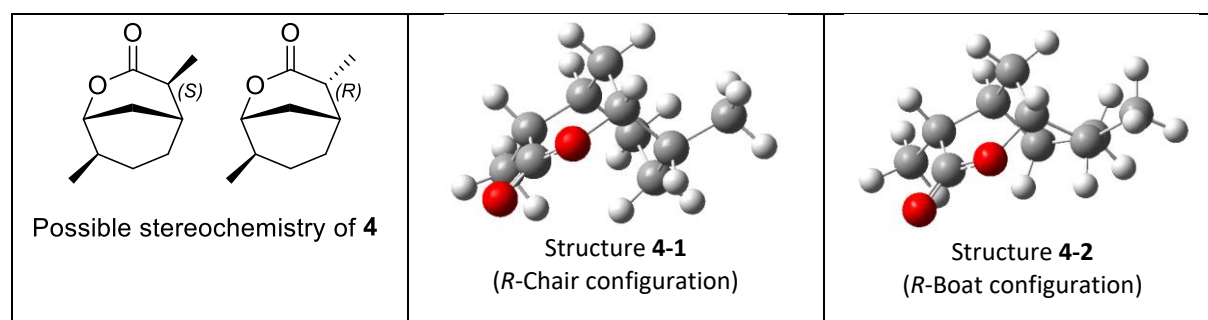
Geometries optimisations were carried out using the M06-2X functional developed by Trulhar and coworkers for applications involving main-group thermochemistry and noncovalent interactions (relevant to the growth of macromolecules), and parametrised only for non-metals.² The calculations were all carried out using the 6-311++g(2d,p) basis set, and a temperature of either 298.15 or 453.15 K (to model respectively the hypothetical ring-opening of lactone **4** at 25 °C, and the polycondensation of **6a** and **6b** at 180 °C). Self-consistent reaction-cavity continuum solvation model (cpcm) was used with ethylacetate as the solvent to model solvation in monomers and in the resulting polyester.³

Full coordinates for all the stationary points, together with computed Gibbs free energy and vibrational frequency data, are available *via* the corresponding Gaussian 09 output files, stored in the digital repository: DOI: 10.6084/m9.figshare.6957368 (private link for review purposes: <https://figshare.com/s/50a0aa5abec69022fd1a>).

DFT calculations related to the formation and to the ring-opening of lactone 4

Lowest energy conformation of lactone 4

Table 3. Computed free Gibbs energies at the rM06-2X/6-311++g(2d,p)/cpcm=ethylethanoate/298K level of theory, for various conformers of lactone 4

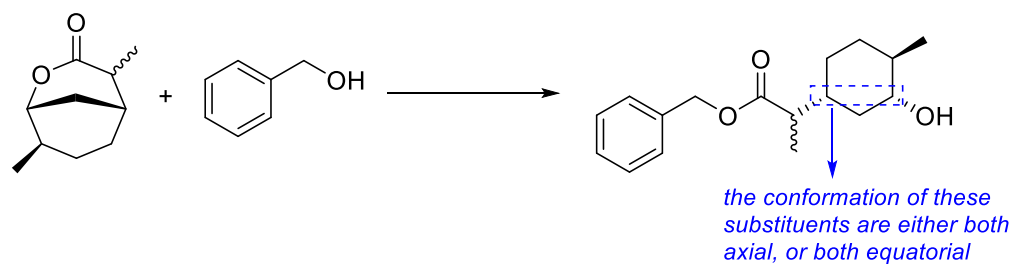


Structure	Stereochemistry (α to C(=O))	Hydrocarbon ring conformation	<i>G</i> (Hartree)	ΔG (kcal mol ⁻¹)
4-1	<i>R</i>	Chair	-540.89703	+0.0 (reference)
4-2	<i>R</i>	Boat	-540.889565	+4.7
4-3	<i>S</i>	Chair	-540.896484	+0.3
4-4	<i>S</i>	Boat	-540.889649	+4.6

Ring-opening reaction of lactone **4**

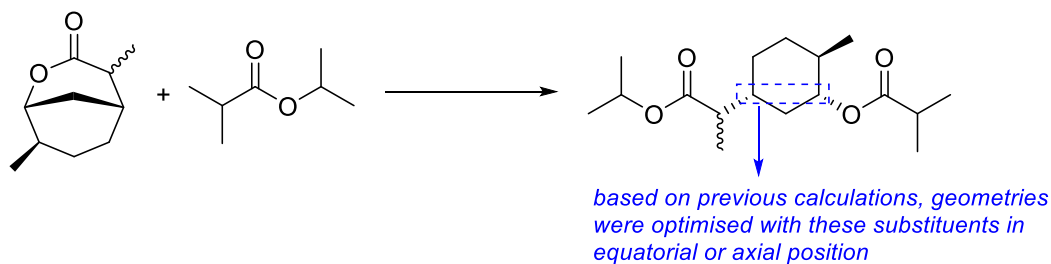
The structures of **4** were taken as the lowest calculated in Table 3 (structures 4-1 and 4-3 for stereoisomer *R* and *S*, respectively).

Table 4. Computed free Gibbs energies at the rM06-2X/6-311++g(2d,p)/cpcm=ethylethanoate/298.15K level of theory, for the ring-opening of lactone **4** by benzyl alcohol.



Structure	Conformation of ring substituents	G (Hartree)	ΔG (kcal mol ⁻¹)
Benzyl alcohol	-	-346.632287	
(<i>R</i>)- 4 (4-1)	-	-540.89703	
(<i>S</i>)- 4 (4-3)	-	-540.896484	
Reference for (<i>R</i>)- 4	-	-887.529317	+0.0
Benzyl ester of ring-opened (<i>R</i>)- 4	axial	-887.521039	+5.2
Benzyl ester of ring-opened (<i>R</i>)- 4	equatorial	-887.527113	+1.4
Reference for (<i>S</i>)- 4	-	-887.528771	+0.0
Benzyl ester of ring-opened (<i>S</i>)- 4	axial	-887.519581	+5.8
Benzyl ester of ring-opened (<i>S</i>)- 4	equatorial	-887.525055	+2.3

Table 5. Computed enthalpies at the rM06-2X/6-311++g(2d,p)/cpcm=ethylethanoate/298.15K level of theory, for the isodesmic reactions between isopropylisopropanoate and lactone **4**.



Structure	Ring substituents position	H (Hartree)	G (Hartree)	ΔH (kcal mol ⁻¹)	ΔG (kcal mol ⁻¹)
Isopropyl-isopropanoate		-425.378255	-425.426797		
(R)- 4 (4-1)		-540.849962	-540.89703		
(S)- 4 (4-3)		-540.848921	-540.896484		
Reference for (R)- 4		-966.228217	-966.323827	+0.0	+0.0
Diester from (R)- 4	Equatorial	-966.2409	-966.319751	-8.0	+2.6
Diester from (R)- 4	Axial	-966.235765	-966.31443	-4.7	+5.9
Reference for (S)- 4		-966.227176	-966.323281	+0.0	+0.0
Diester from (S)- 4	Equatorial	-966.239354	-966.318842	-7.6	+2.8
Diester from (S)- 4	Axial	-966.236292	-966.314569	-5.7	+5.5

Reaction of lactonisation of 6a into 4

For simplicity, calculations were only carried out on the stereoisomers with a (*R*)-configuration in α of the carbonyl groups (either carboxylic acid in **6a**, or lactone in **4**).

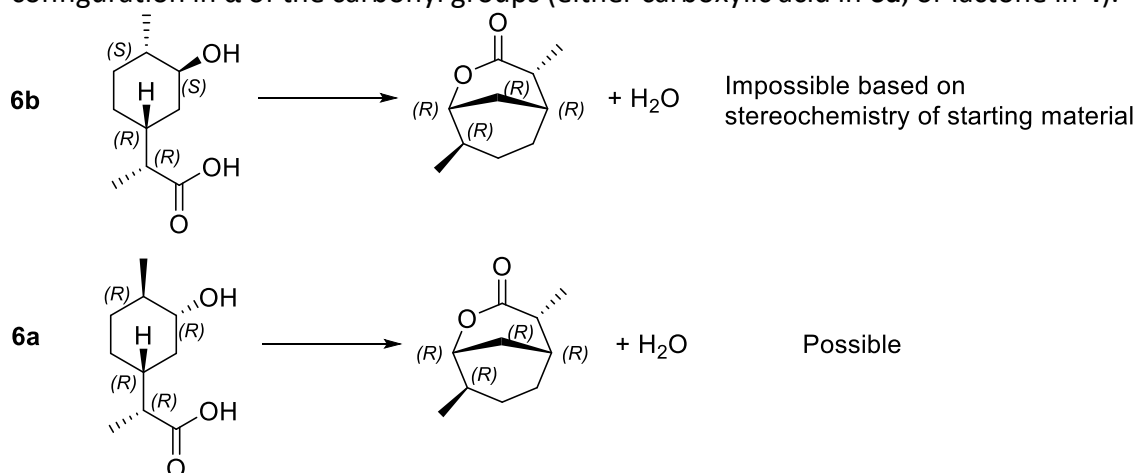


Table 6. Computed free Gibbs energies at the rM06-2X/6-311++g(2d,p)/cpcm=ethylethanoate/453.15K level of theory, for the lactonisation of **6a** into **4**.

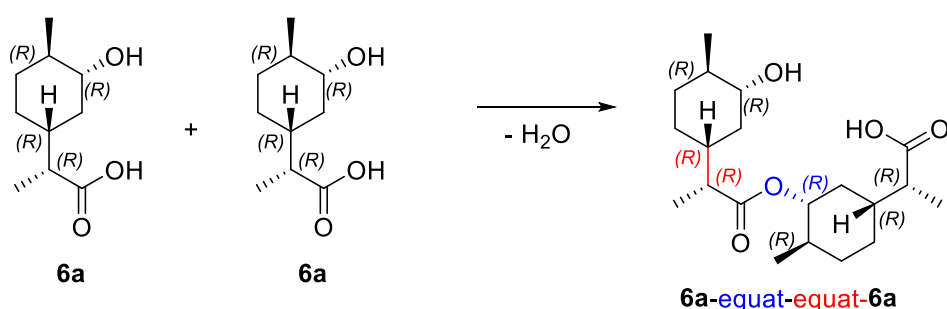
Structure	Conformation of ring substituents	G (Hartree)	ΔG (kcal mol ⁻¹)
(2- <i>R</i>)- 6a	All equatorial (chair conformation)	-617.349972	+0.0
(2- <i>R</i>)- 6a	All axial (chair conformation)	-617.345053	+3.1
(2- <i>R</i>)- 6a	All axial (boat conformation)	-617.337729	+7.7
H ₂ O	-	-76.436954	
Reference (2- <i>R</i>)- 6a – H ₂ O	-	-540.913018	+0.0
(<i>R</i>)- 4 (4-1 from Table S1)	-	-540.926242	-8.3

Reaction of condensation of 6a and 6b

For simplicity, calculations were only carried out on the stereoisomers with a (*R*)-configuration in α of the carboxylic acid groups in **6a/b**.

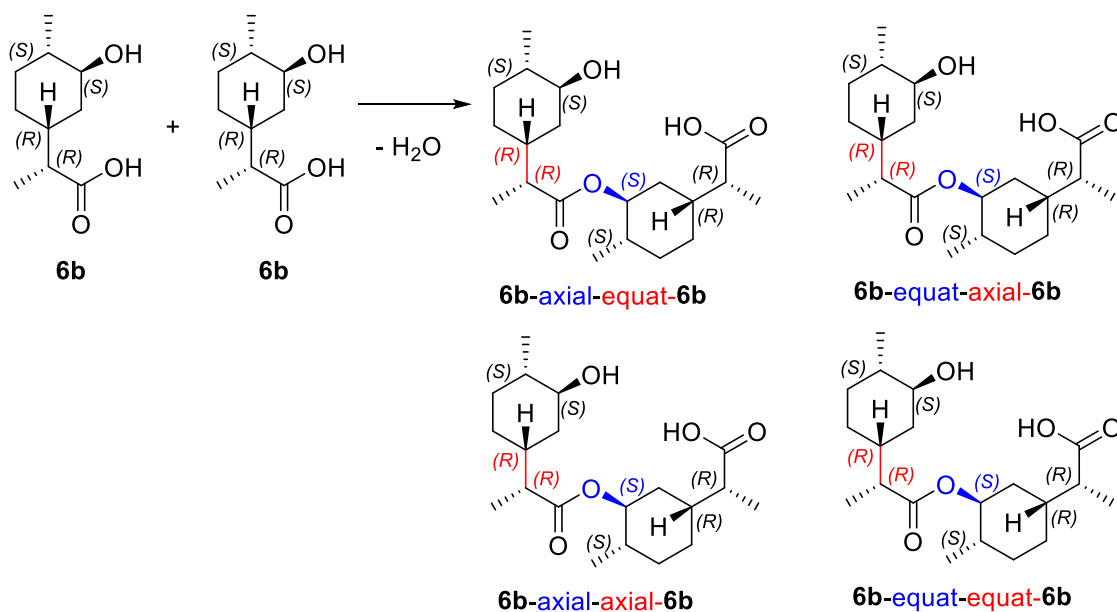
For nomenclature purposes, the polymer chains are considered to grow from the alcohol moiety (ie in the direction OH \rightarrow COOH), and polymers (here dimers) are named Monomer 1-configuration of the acid group of Monomer 1(equatorial/axial)-configuration of the alcohol group of Monomer 2(equatorial/axial)-Monomer 2 (for example **6a-equat-equat-6a**, see below for graphical representation).

Homopolymerisation of 6a



The dimer **6a-axial-axial-6a** was not calculated based on steric and energetic considerations (**6a** in boat form, with acid and alcohol groups in axial is not favoured, see Table 6).

Homopolymerisation of 6b



Copolymerisation of **6a** and **6b**

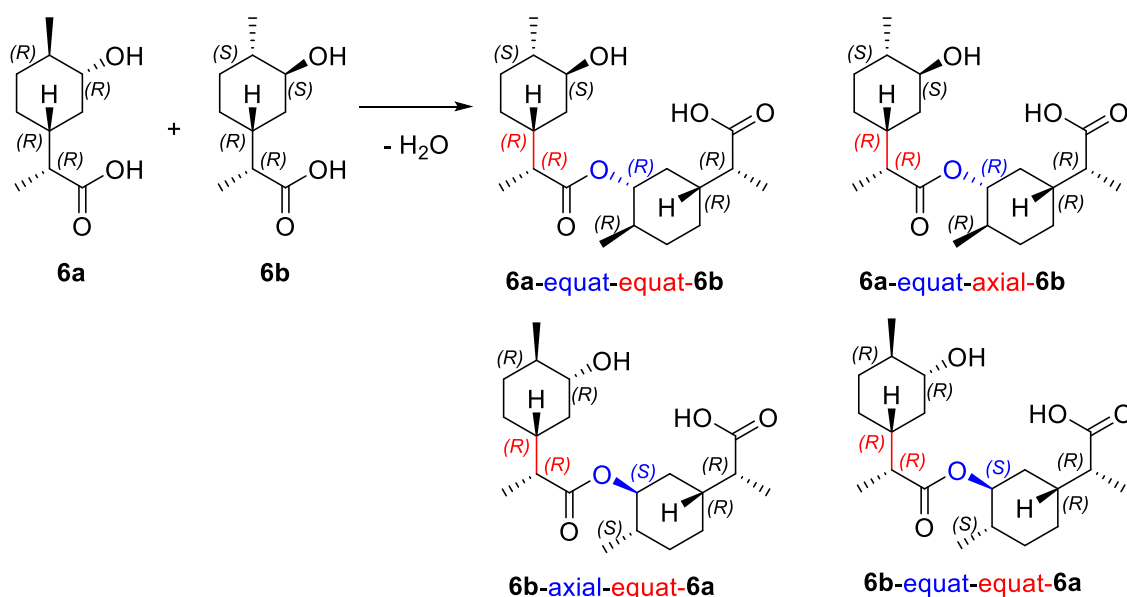


Table 7. Computed free Gibbs energies at the rM06-2X/6-311++g(2d,p)/cpcm=ethylethanoate/453.15K level of theory, for the lactonisation of **6a** into **4**.

Structure	<i>G</i> (Hartree)	ΔG (kcal mol ⁻¹)
(2- <i>R</i>)- 6a (all substituents in equatorial)	-617.349972	+0.0 (Ref)
(2- <i>R</i>)- 6a (all substituents in axial)	-617.345053	+3.1
(2- <i>R</i>)- 6b (alcohol in axial, acid group in equatorial)	-617.348092	+1.2
(2- <i>R</i>)- 6b (alcohol in equatorial, acid group in axial)	-617.346959	+1.9
H ₂ O	-76.436954	
Reference homopolymerisation of (2- <i>R</i>)- 6a (2 × (2- <i>R</i>)- 6a – H ₂ O)	-1158.26299	+0.0
6a-equat-equat-6a	-1158.264488	-0.9
Reference homopolymerisation of (2- <i>R</i>)- 6b (2 × (2- <i>R</i>)- 6b – H ₂ O)	-1158.25923	+0.0
6b-axial-equat-6b	-1158.259696	-0.3
Reference homopolymerisation of (2- <i>R</i>)- 6b (2 × (2- <i>R</i>)- 6b – H ₂ O)	-1158.256964	+0.0
6b-equat-axial-6b	-1158.258235	-0.8
Reference homopolymerisation of (2- <i>R</i>)- 6b ((2- <i>R</i>)- 6b +(2- <i>R</i>)- 6b – H ₂ O)	-1158.258097	+0.0
6b-axial-axial-6b	-1158.26093	-1.8
6b-equat-equat-6b	-1158.261062	-1.9
Reference copolymerisation of (2- <i>R</i>)- 6b and(2- <i>R</i>)- 6a ((2- <i>R</i>)- 6a +(2- <i>R</i>)- 6b – H ₂ O)	-1158.26111	+0.0
6a-equat-equat-6b	-1158.262504	-0.9
6b-axial-equat-6a	-1158.262652	-1.0
Reference copolymerisation of (2- <i>R</i>)- 6b and(2- <i>R</i>)- 6a ((2- <i>R</i>)- 6a +(2- <i>R</i>)- 6b – H ₂ O)	-1158.259977	+0.0
6a-equat-axial-6b	-1158.261065	-0.7
6b-equat-equat-6a	-1158.266156	-3.9

References

- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.
- 2 Y. Zhao and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2008, **120**, 215-241.
- 3 (a) G. Scalmani and M. J. Frisch, *The Journal of Chemical Physics*, 2010, **132**, 114110; (b) D. M. York and M. Karplus, *The Journal of Physical Chemistry A*, 1999, **103**, 11060-11079.