Electronic Supplementary Information

Ring opening polymerization of lactides and lactones by multimetallic alkyl zinc complexes derived from the acids Ph₂C(X)CO₂H (X = OH, NH₂)

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Redshaw 1997

Gibson 1997

Redshaw 2007

Redshaw 2011 (M= Cu, Zn)

Redshaw 2009

Redshaw 2005
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Crystallography

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Figure S5. Alternative view of 3.
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**Ring opening polymerisation**

**Table S1.** Optimum condition screening for the ROP of \(\varepsilon\)-CL, \(r\)-LA and \(\delta\)-VL using 4.

| Run | Monomer | \([\text{Monomer}]:[\text{Cat}]:[\text{OH}]\) | Time/h | Temp/°C | Conv\(^a\) | \(M_n\)^b × 10\(^3\),GPC | \(M_n\),Cal\(^c\) | PDI\(^d\)  |
|-----|---------|---------------------------------|--------|---------|----------|-----------------|----------------|------|
| 1   | \(\varepsilon\)-CL | 125:1:0                        | 1      | 110     | 91       | 11400           | 12980          | 1.40 |
| 2   | \(\varepsilon\)-CL | 250:1:0                        | 1      | 110     | 78       | 15000           | 22260          | 1.38 |
| 3   | \(\varepsilon\)-CL | 375:1:0                        | 1      | 110     | 88       | 20800           | 37670          | 1.41 |
| 4   | \(\varepsilon\)-CL | 500:1:0                        | 1      | 110     | 91       | 33700           | 51930          | 1.68 |
| 5   | \(\varepsilon\)-CL | 625:1:0                        | 1      | 110     | 85       | 43800           | 60640          | 1.43 |
| 6   | \(\varepsilon\)-CL | 750:1:0                        | 1      | 110     | 89       | 56200           | 76190          | 1.51 |
| 7   | \(\varepsilon\)-CL | 250:1:0                        | 3      | 80      | 69       | 8590           | 19690          | 1.21 |
| 8   | \(\varepsilon\)-CL | 250:1:0                        | 3      | 60      | 22       | 3850           | 6280          | 1.09 |
| 9   | \(\varepsilon\)-CL | 250:1:0                        | 3      | 25      | ---      | ---           | ---            | --- |
| 10  | \(\varepsilon\)-CL | 250:1:1                        | 1      | 110     | 67       | 2580           | 19230          | 1.10 |
| 11  | \(r\)-LA   | 50:1:0                         | 12     | 110     | 74       | 3370           | 5330          | 1.19 |
| 12  | \(r\)-LA   | 100:1:0                        | 12     | 110     | 67       | 6150           | 9660          | 1.23 |
| 13  | \(r\)-LA   | 150:1:0                        | 12     | 110     | 61       | 9670           | 13190         | 1.27 |
| 14  | \(r\)-LA   | 200:1:0                        | 12     | 110     | 65       | 13000          | 18740         | 1.51 |
| 15  | \(r\)-LA   | 250:1:0                        | 12     | 110     | 60       | 15400          | 21620         | 1.37 |
| 16  | \(r\)-LA   | 300:1:0                        | 12     | 110     | 64       | 22900          | 27670         | 1.40 |
| 17  | \(r\)-LA   | 150:1:0                        | 12     | 80      | 19       | 1460           | 4110          | 1.09 |
| 18  | \(\delta\)-VL | 50:1:0                         | 24     | 110     | 42       | 860            | 2100          | 1.04 |
| 19  | \(\delta\)-VL | 100:1:0                        | 24     | 110     | 58       | 2670           | 5810          | 1.13 |
| 20  | \(\delta\)-VL | 150:1:0                        | 24     | 110     | 41       | 3210           | 6160          | 1.23 |
| 21  | \(\delta\)-VL | 200:1:0                        | 24     | 110     | 31       | 4750           | 6210          | 1.08 |
| 22  | \(\delta\)-VL | 250:1:0                        | 24     | 110     | 51       | 5800           | 12770         | 1.25 |
| 23  | \(\delta\)-VL | 300:1:0                        | 24     | 110     | 60       | 8820           | 18020         | 1.12 |

\(^a\) Determined by \(^1\)H NMR spectroscopy; \(^b\) Calculated from \([(\text{Monomer})_0]/[\text{Cat}]_0 \times \text{conv.} \times \text{Monomer molecular weight}; \(^c\) \(M_n\) from GPC. \(^d\) From GPC.
Figure S10. Relationship between $[\text{CL}]/[4]$ and the number of average molecular weight and PDI of the polymer.
Figure S11. $^1$H NMR spectrum of polycaprolactone (run 1 table 1).
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