

Supporting Information for

Degradable branched and cross-linked polyesters from a

bis(1,3-dioxolan-4-one) core

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Table S1. Gel contents for bisDOX and 1,4-butanediol co-polymers synthesised with different catalysts.

Entry	Catalyst	Gel (%)
1	H,H[Al]Me	5
2	tBu, tBu[Al]Me	8
3	Sn(oct)_2	93

All co-polymerisations were conducted at 120 °C neat for 18 h where [bisDOX]:[1,4-butanediol]:[catalyst] = 50:50:1.

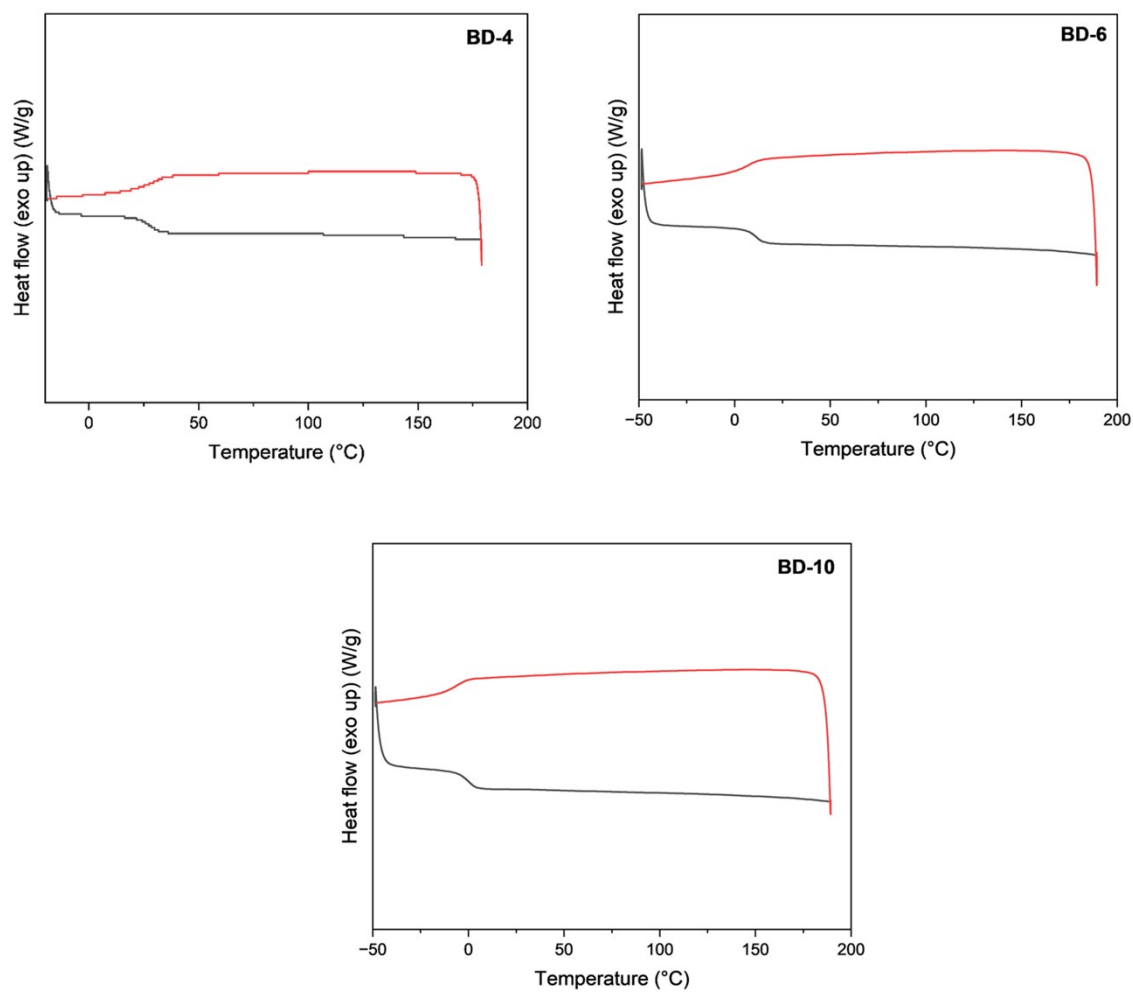


Figure S1. DSC thermograms showing first cooling (red) and second heating (black) ramps for cross-linked polyesters, BD-4, BD-6 and BD-10.

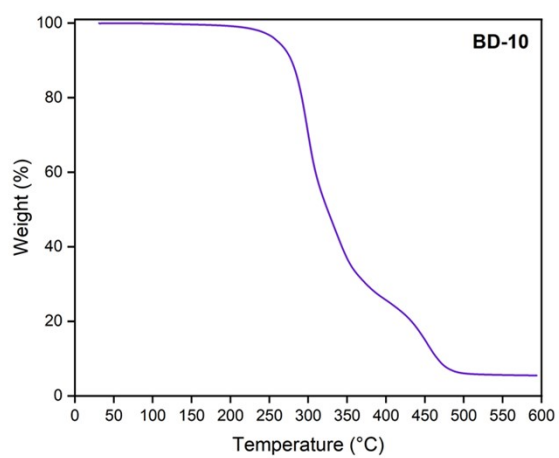
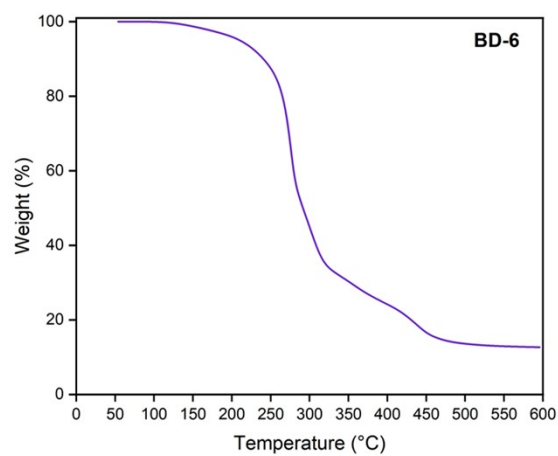
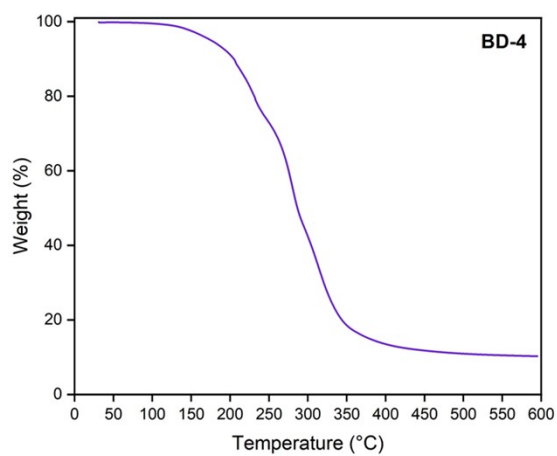


Figure S2. TGA thermograms for BD-X samples.

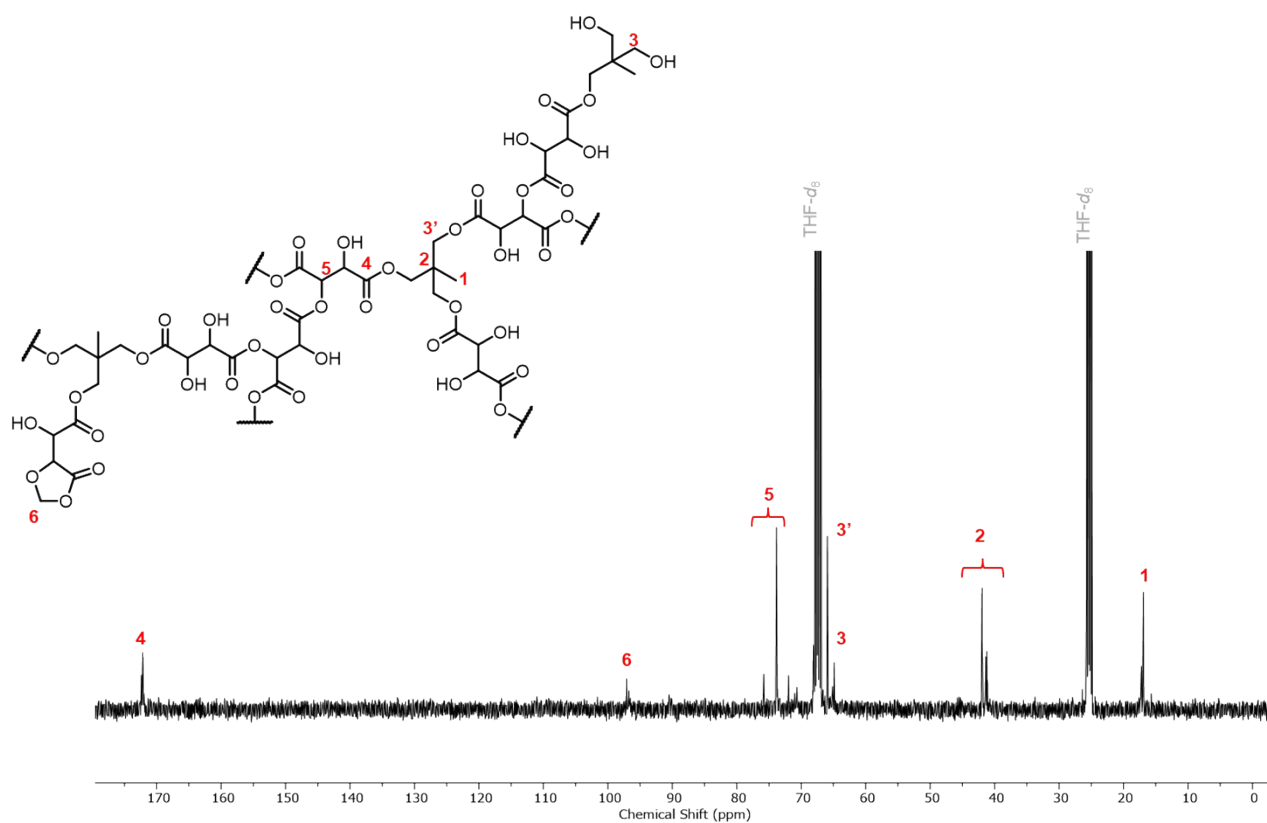


Figure S3. ^{13}C NMR (THF- d_6 , 298 K, 125 MHz) of branched bisDOX and TME co-polymer.

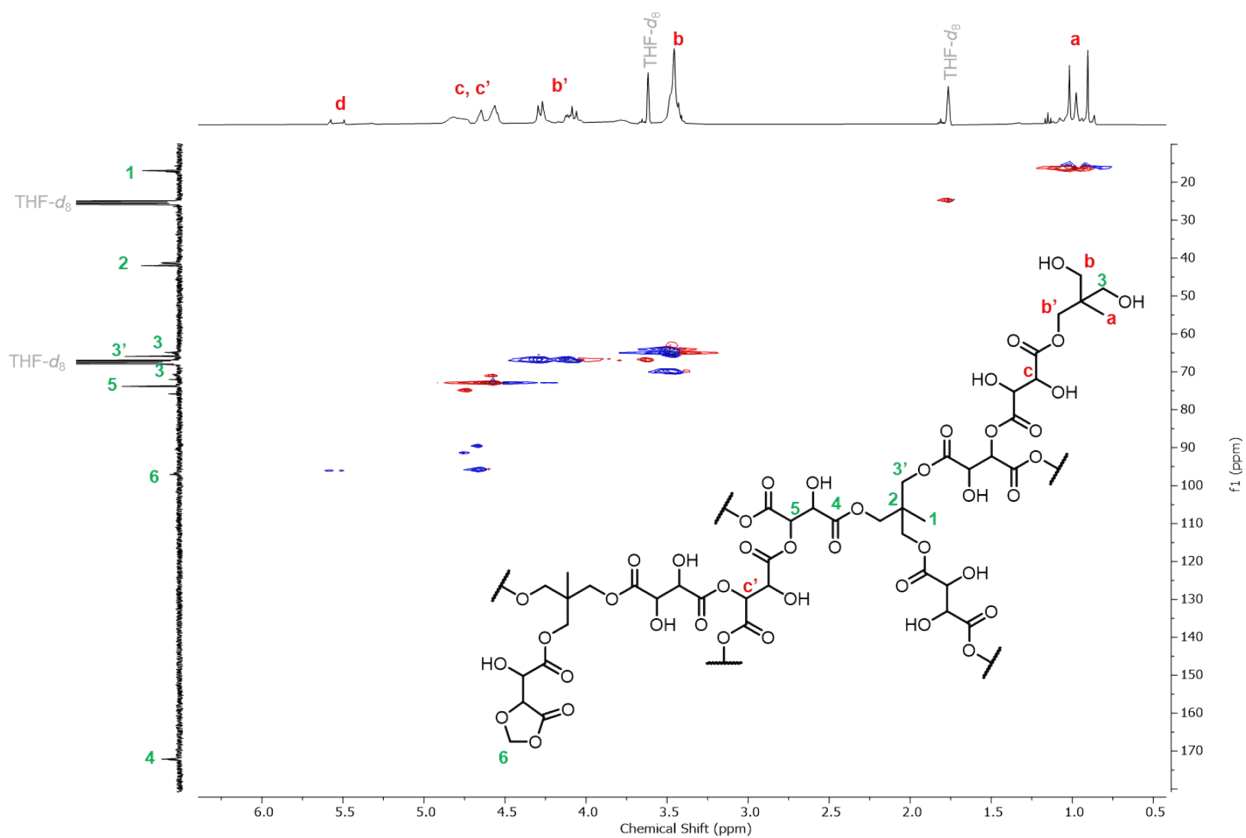


Figure S4. ^1H - ^{13}C HSQC NMR (THF- d_6 , 298 K, 125 MHz) of branched bisDOX and TME co-polymer.

Figure S6. Overlaid normalised FT-IR spectra of BD-X cross-linked polyesters, with inset showing the carbonyl region. The peak at 1800 cm^{-1} is attributed to the C=O stretch of pendant bisDOX rings.

Determination of Degree of Branching of bisDOX-TME polymer

Branched polymers can be characterised by their degree of branching (DB), a quantitative measure of the extent of branching. A linear polymer (ignoring end groups) would have $DB = 0$, whilst for a perfect dendrimer, $DB = 1$. DB is commonly determined by NMR spectroscopy in which the signal intensities for peaks corresponding to dendritic (D), linear (L) and terminal (T) units are measured and compared. A nominal degree of branching was calculated to evidence the branched character of the bisDOX-TME co-polymer (Table 2, Entry 5 in main manuscript) using the equation $DB = 2D / (2D + L)$.¹ DB was determined by the relative integration values for the methine peaks corresponding to the di- and tri-substituted TME units within the polymer (Figure 1 main manuscript, peaks denoted a' and a'', respectively) and was found to be 0.66. This value is indicative of a hyperbranched polymer, however, the added structural complexity from the tetrafunctional bisDOX units means the absolute degree of branching may not be represented by this figure.

Additional pictures of cross-linked polyester films

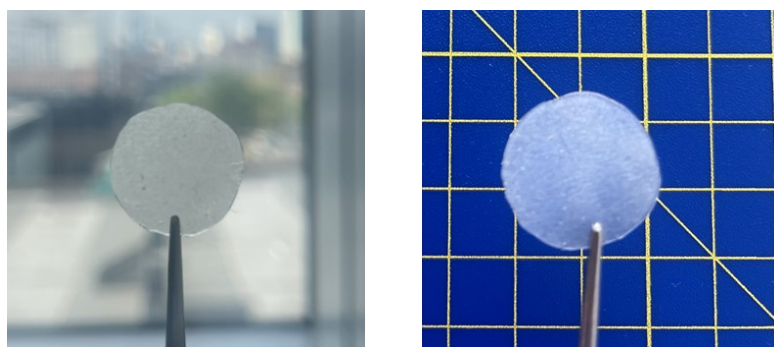
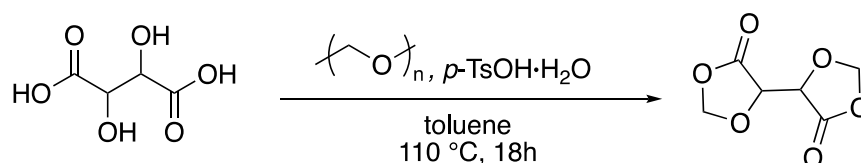


Figure S7. Additional pictures of BD-10 polymer films.

Additional Synthetic Procedures



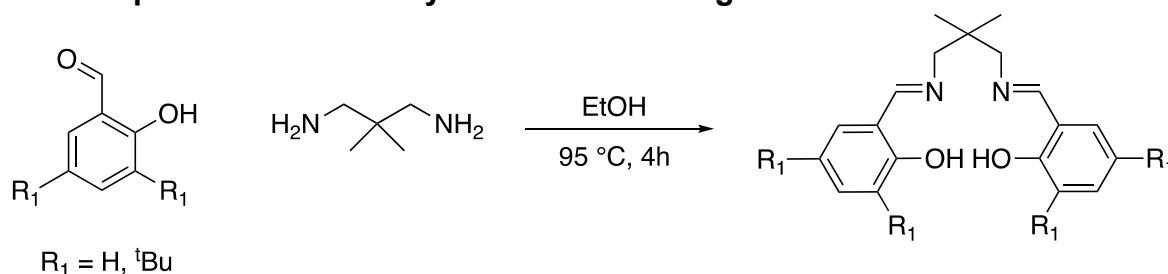
Synthesis of bisDOX

Scheme S1. Synthesis of bisDOX.

BisDOX was synthesised according to literature.² *L*-tartaric acid (100 mmol, 1.0 equiv., 15.01 g), paraformaldehyde (240 mmol, 2.4 equiv., 7.21 g) and $p\text{-TsOH}\cdot\text{H}_2\text{O}$ (20 mmol, 0.2 equiv., 3.80 g) were dissolved in toluene (250 mL) and activated molecular sieves (4 Å) were added. The reaction mixture was heated at reflux for 18h. Upon cooling, the mixture was filtered to remove sieves, diluted with EtOAc (100 mL) and washed with saturated NaHCO_3 solution (3 x 150 mL), DI water (150 mL) and saturated NaCl solution (150 mL). The organic phase was dried over MgSO_4 and the solvent was removed under reduced pressure. The crude product was dissolved in THF and precipitated from hexane to give white crystals (4.96 g, 28%).

^1H NMR (THF- d_8 , 500 MHz): δ 5.54 (s, 2H), 5.47 (s, 2H), 4.71 (s, 2H). ^{13}C NMR (126 MHz, THF) δ 169.67, 96.64, 73.31

General procedure for the synthesis of Salen ligands



Scheme S2. Synthesis of Salen ligands.

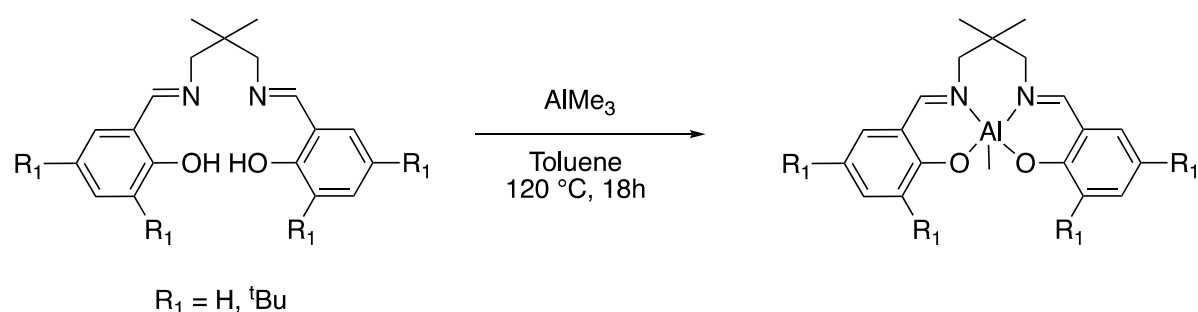
This procedure was adapted from the literature.³ A solution of 2,2-dimethyl-1,3-propanediamine (45 mmol, 1.0 equiv) in ethanol was added dropwise to a stirring solution of

the corresponding aldehyde (22.5 mmol, 0.5 equiv) in ethanol at room temperature. The reaction was heated to reflux and stirred for 3 h before cooling in an ice bath. The precipitated product was collected by filtration, washed with cold methanol, and dried under vacuum.

R¹=H: ¹H NMR (400 MHz, CDCl₃) δ 13.55 (s, 2H), 8.34 (d, *J* = 1.4 Hz, 2H), 7.37 – 7.20 (m, 4H), 7.00 – 6.85 (m, 4H), 3.50 (d, *J* = 1.3 Hz, 4H), 1.08 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 165.79, 161.24, 132.41, 131.41, 118.67, 116.99, 68.11, 36.28, 24.40.

R¹=^tBu: ¹H NMR (400 MHz, CDCl₃) δ 13.79 (s, 2H), 8.39 (s, 2H), 7.40 (s, 2H), 7.13 (s, 2H), 3.49 (s, 8H), 1.46 (s, 18H), 1.31 (s, 18H), 1.11 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 166.61, 158.24, 140.17, 136.81, 127.03, 125.97, 117.56, 88.35, 35.18, 34.27, 31.64, 29.56.

General procedure for the synthesis of Al (salen) catalysts



Scheme S3. Synthesis of aluminium salen catalysts.

This procedure was adapted from the literature.³ In a glovebox, to a solution of the Salen ligand (6.5 mmol, 1.0 equiv) in toluene was added AlMe₃ (2.0 M in toluene) (6.5 mmol, 1.0 equiv) dropwise. The Schlenk flask was sealed, removed from the glovebox and heated at 110 °C in an oil bath overnight. The flask was cooled in an ice bath and solvent removed *via* cannula transfer and the product washed with anhydrous toluene (3 x 20 mL) before drying *in vacuo*.

R¹= H: ^{H,H}[Al]Me ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 2H), 7.29 (ddd, *J* = 8.7, 7.1, 1.9 Hz, 2H), 7.11 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.93 (dd, *J* = 8.5, 1.1 Hz, 2H), 6.64 (ddd, *J* = 7.9, 7.1, 1.1 Hz, 2H), 3.77 (d, *J* = 12.1, 2H), 3.17 (d, *J* = 12.1 Hz, 2H), 1.07 (s, 3H), 0.91 (s, 3H), -0.88 (s, 3H).

R¹ = ^tBu: ^tBu,^tBu[Al]Me ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 2H), 7.49 (d, *J* = 2.6 Hz, 2H), 7.03 (d, *J* = 2.6 Hz, 2H), 3.40 (d, *J* = 12.0 Hz, 2H), 3.29 (d, *J* = 12.0 Hz, 2H), 1.49 (s, 18H), 1.31 (s, 18H), 1.15 (s, 3H), 1.04 (s, H), -1.07 (s, 3H).

References

1. H. Frey and D. Höltel, *Acta Polymerica*, 1999, **50**, 67-76.
2. T. Şucu, M. Wang and M. P. Shaver, *Macromolecules*, 2023, **56**, 1625-1632.
3. P. Hornnirun, E. L. Marshall, V. C. Gibson, R. I. Pught and A. J. P. White, *Proceedings of the National Academy of Science U. S. A.*, 2006, **103**, 15343-15348.