Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information For:

# High Elasticity, Chemically Recyclable, Thermoplastics From Bio-based Monomers: Carbon Dioxide, Limonene Oxide and ε-Decalactone

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## Experimental Section

## 1. General Methods

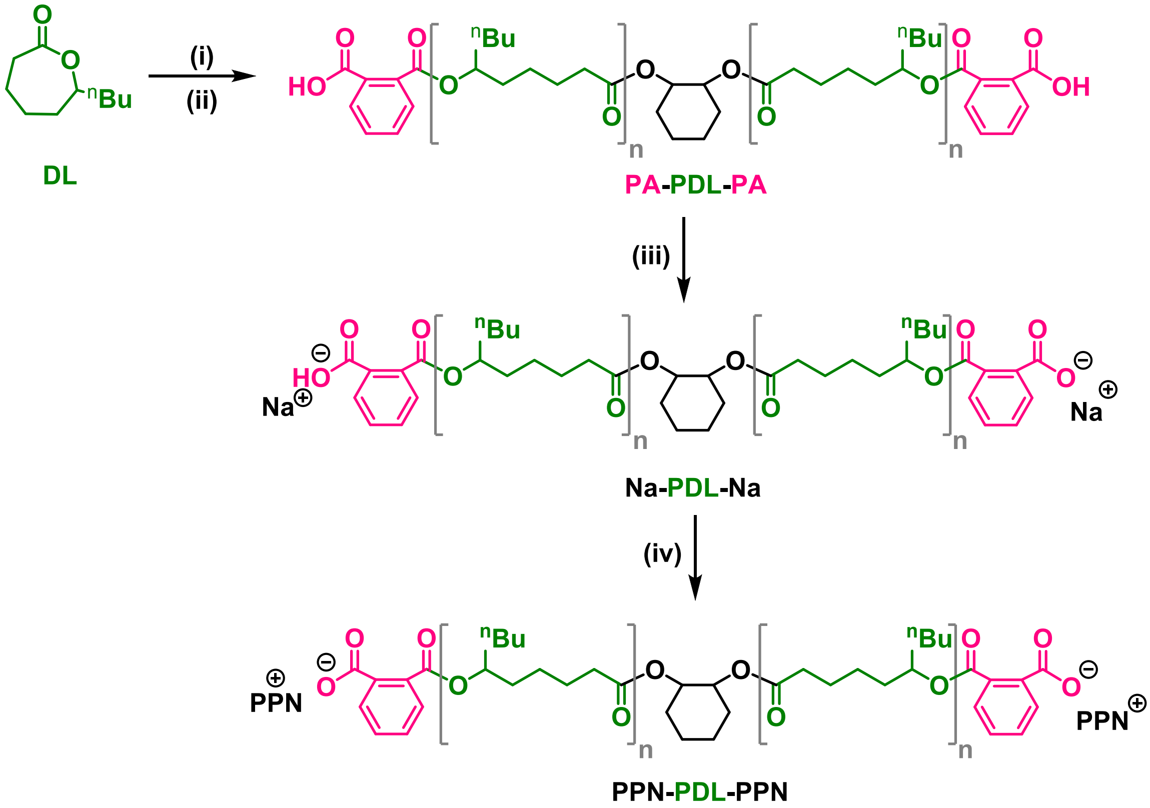
**NMR**: spectra were obtained using a Bruker AV 400 instrument.
**Size Exclusion Chromatography (SEC):** obtained using a Shimadzu LC-20AD instrument, with HPLC grade THF as the eluent, flowing at 1.0 mL/min, at 30 °C and using monodisperse polystyrene standards for instrument calibration.
**Differential Scanning Calorimetry (DSC):** Recorded for precipitated polymer samples on a Mettler Toledo DSC3 Star calorimeter, under a $N_2$ flow (80 mL $min^{-1}$). Samples were heated, at a rate of 10 °C $min^{-1}$, from -80 to +170 °C. Glass transition temperatures ($T_g$) were determined from the midpoint of the transition in the second heating curve.
**Dynamic Mechanical Thermal Analysis (DMTA):** Recorded on TA instruments RSA-G2 Solids Analyser, at 1 Hz frequency and 5 °C $min^{-1}$ heating rate.
**Thermal Gravimetric Analysis (TGA):** Measured on Mettler-Toledo Ltd TGA/DSC 1 system. Powder polymer samples were heated from 30 to 500 °C, at a rate of 10 °C $min^{-1}$, under $N_2$ flow (100 mL $min^{-1}$).
**Tensile mechanical tests:** carried out using an EZ-LX Universal Testing Instrument (Shimadzu). Dumbbell shaped specimens were cut using a Zwick ZCP020 cutting press, equipped with a cutting device for ISO 527-2, type 5B. Uniaxial extension experiments (10 mm $min^{-1}$ cross-head speed) were run according to ISO 527.

## Materials

All solvents and reagents were purchased and used as obtained from commercial sources (Sigma Aldrich), unless stated otherwise. The synthesis of [$H_2L$] macrocyclic ligand, was carried out in air and performed according to literature procedures.[1] The synthesis of the catalyst, [$LZn_2(Ph)_2$] (**1**) and [$Al^{MeMe}$] (**2**), were carried out under inert conditions according to literature procedures.[2, 3] Bis(triphenylphosphine)iminium iodide (PPNI) was synthesised according to its literature procedure.[4] Limonene oxide (LO) was purified by first stirring over NaH, followed by addition of MeI, and fractional distillation at 40 °C (1 mbar). This procedure was repeated twice more (three distillations in total), and the LO was stored under a nitrogen atmosphere. ε-Decalactone (DL) was dried over $CaH_2$, distilled under reduced pressure twice and stored under a nitrogen atmosphere. *Trans*-1,2-cyclohexanediol (CHD) was recrystallized from ethyl acetate and stored under nitrogen. Research-grade $CO_2$ was dried through two drying columns (VICI, Model number: P600-1) in series before use.

## 2. Procedures

### Synthesis of $[PPN]_2[PDL]$



**Scheme S1.** Reaction conditions for the synthesis of $[PPN]_2[PDL]$: Part (a) Synthesis of PA-PDL-PA (i) **1**, CHD, DL, 2 h, 100 °C toluene. (ii) PA, 16 h, 100 °C, molar ratio: [**1**]/[CHD]/[PA]/[DL] = 1/4/100/350-1000. Part (b) end group modification of PA-PDL-PA (iii) NaOH, 2 h, 25 °C, chloroform. (iv) PPNI, 2 h, 40 °C. Molar ratio: [diacid end group]/[NaOH]/[PPNI] = 1/1/1.

### Synthesis of PA-PDL-PA ((i) and (ii) in Scheme S1)

Under anaerobic conditions, $[LZn_2Ph_2]$, **1**, (40 mg, 40 µmol, 1.0 equiv.), CHD (21 mg, 0.2 mmol, 4 equiv.), DL (2.8 - 8.2 g, 17 - 47 mmol, 350 - 1000 equiv.) were added to a vial, with toluene (7.5 mL), and the solution was heated to 100 °C, with stirring for 2.0 h. After the formation of PDL, PA (0.7 g, 47 mmol, 100 equiv.) was added and the reaction was heated at 100 °C, for 16 h. The reaction was monitored by aliquot removal and subsequent analysis using $^{31}P\{^1H\}$ NMR spectroscopy end-group titration (see below) to ensure all PDL hydroxyl end groups were converted to di-acids. The reaction was then quenched, by exposure to air, and the excess PA was removed by extraction with hot water. The crude sample, dissolved in toluene, was dried ($Na_2SO_4$), before being purified by pouring the solution into cold MeOH ( -78 °C) to induce polymer precipitation. The product polymer was collected, dried and analysed by $^1H$ NMR spectroscopy and SEC analysis (THF as eluent, 1 mL min$^{-1}$, 30 °C).

### PA-PDL-PA end group deprotonation and cation exchange ((iii) and (iv) in Scheme S1)

The di-acid terminated PDL was then dissolved in $CHCl_3$ and titrated with NaOH (1M), using phenolphthalein as the indicator. Once the base addition was complete, the reaction was stirred for an additional 2 h at 25 °C to form Na-PDL-Na. PPNI (equimolar to the amount of NaOH added) was then added and the solution was stirred at 40 °C, for 2 h. The sample was purified by precipitation into a cold methanol solution (-78 °C) three times; the product polymer was dried under vacuum and analysed by $^{1}H$ NMR spectroscopy and SEC analysis (THF as eluent, 1 mL min$^{-1}$, 30 °C).

### Ring-opening copolymerization of LO and $CO_2$ using $[PPN]_2[PDL]$ as initiator

Under anaerobic conditions, [Al$^{MeMe}$] catalyst, **2**, (0.1 g, 0.2 mmol, 1.0 equiv.), $[PPN]_2[PDL]$ (0.25 equiv.) and LO (41 mL, 25 mmol, 125 equiv.) were added to a 25 mL stainless steel Parr reaction vessel. The reactor was heated to 45 °C and pressurised to 20 bar $CO_2$ and allowed to react under static $CO_2$ pressure for 24 h. Thereafter, the vessel was cooled and de-pressurised. The resulting crude polymer was purified by repeat precipitation of a methylene chloride solution into pentane.

### End group analysis by $^{31}P\{^{1}H\}$ NMR spectroscopy

A literature procedure for hydroxyl end group analysis using $^{31}P$ $\{^{1}H\}$ NMR spectroscopy was followed.[5] A mixture of a stock solution (40 µL), excess 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (40 µL) and the polymer sample (20 mg) was added to an NMR tube and shaken. The mixture was allowed to react for 6 h before spectra were measured. The stock solution consists of bisphenol A (400 mg) and of $[Cr(acac)_3]$ (5.5 mg), in pyridine (10 mL).

### Depolymerization of PLC

In a nitrogen filled glovebox, a sample of triblock polymer (100 mg) was dissolved in anhydrous toluene (5 mL), before catalyst **1** (1.6 mM) was added. The vial, equipped with a magnetic stirrer bar, was sealed and placed in an oil bath, pre-heated to 80 °C. At specific time intervals, the vial was quenched to 0 °C, in an ice-water bath, before being taken into a nitrogen filled glovebox and an aliquot removed for NMR spectroscopy and SEC analysis.

### Degradation of PDL

*p*-toluenesulfonic acid.$H_2O$ (PTSA) (10 mg, 0.05 mmol) was added to a solution of residual PDL (50 mg, from the depolymerization of PLC) in THF (5 mL) and heated with stirring to 60 $^{o}$C. SEC analysis was done on aliquots were taken at regular intervals to track the degradation progress.

## 3. SEC Data showing the bimodal molar mass distribution from chloride and diol initiators

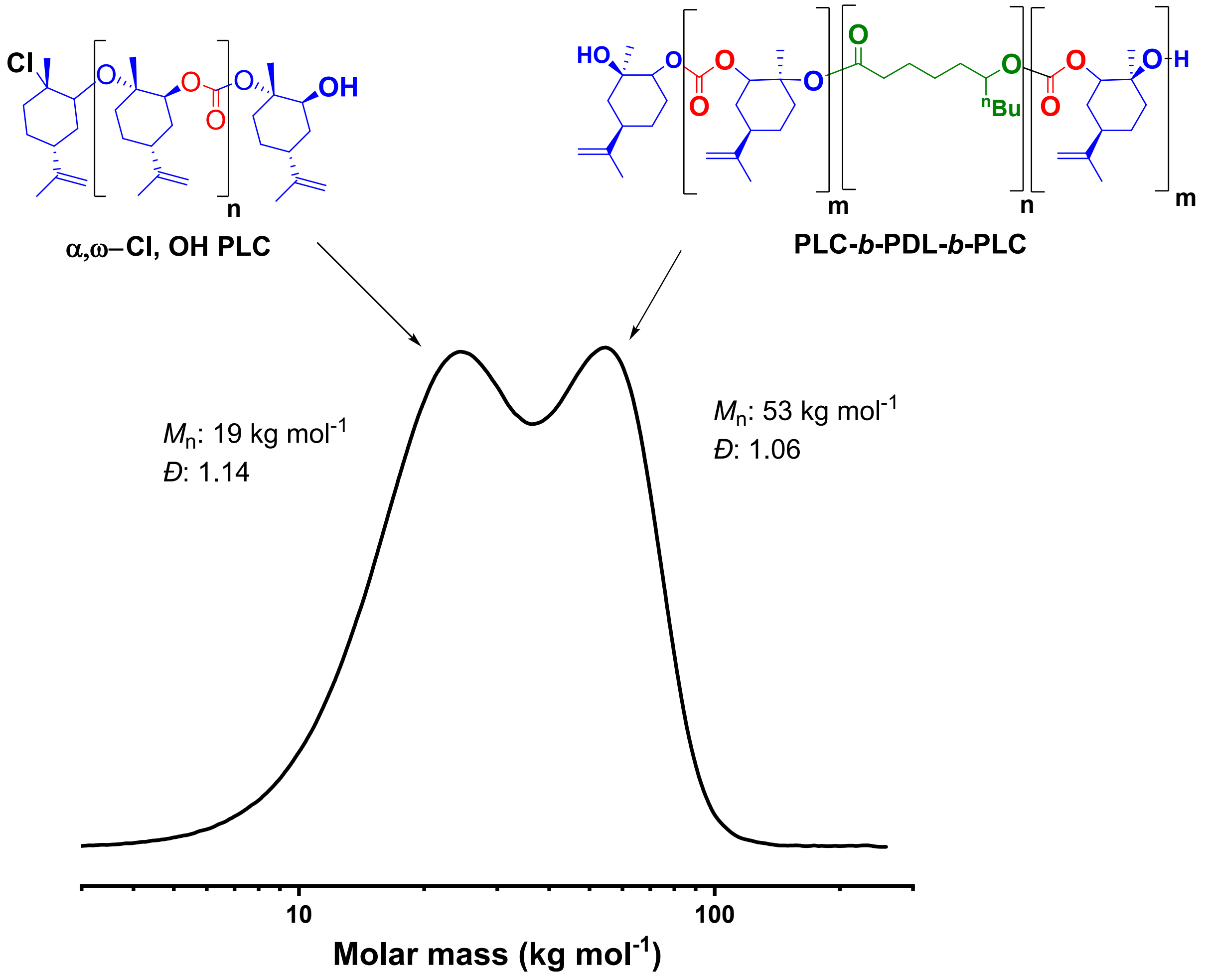


**Fig. S1.** SEC trace showing bimodal molar mass distributions resulting from the ROCOP of LO/$CO_2$ using **2** in the presence of PPNCl and PDL.

## 4. NMR Characterization Data

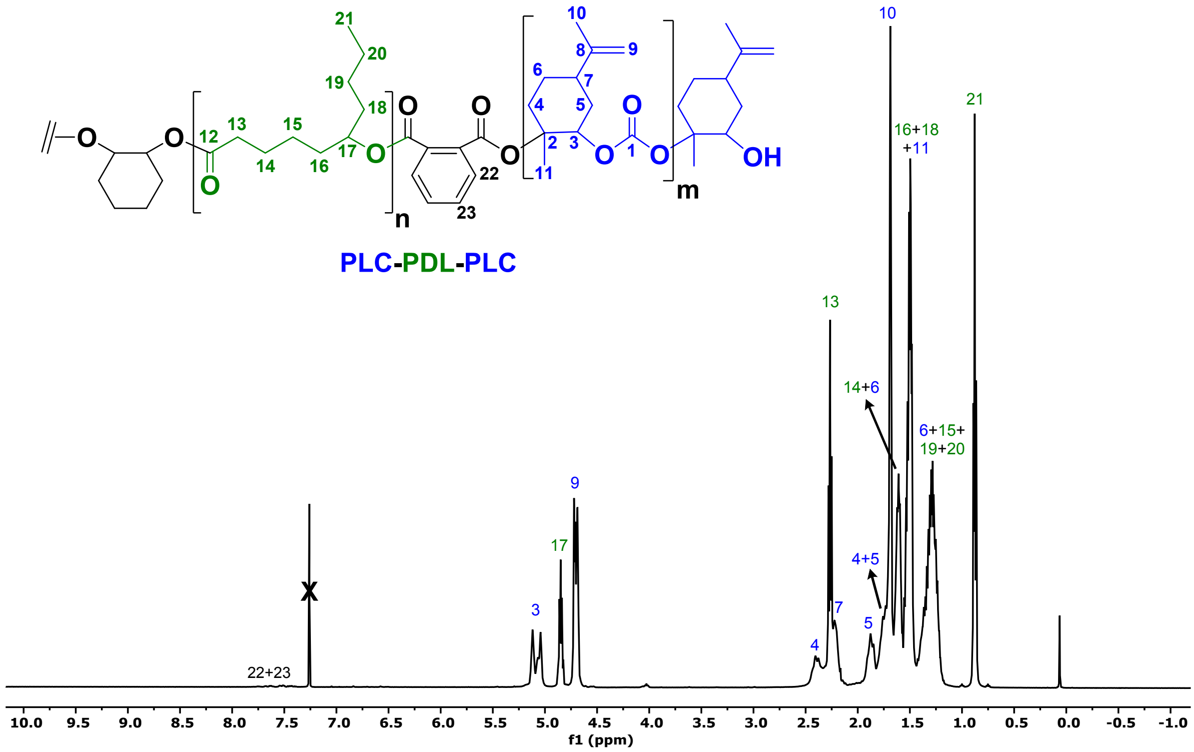


**Fig. S2** $^{1}$H NMR spectrum of PLC-*b*-PDL-*b*-PLC (in CDCl$_3$).

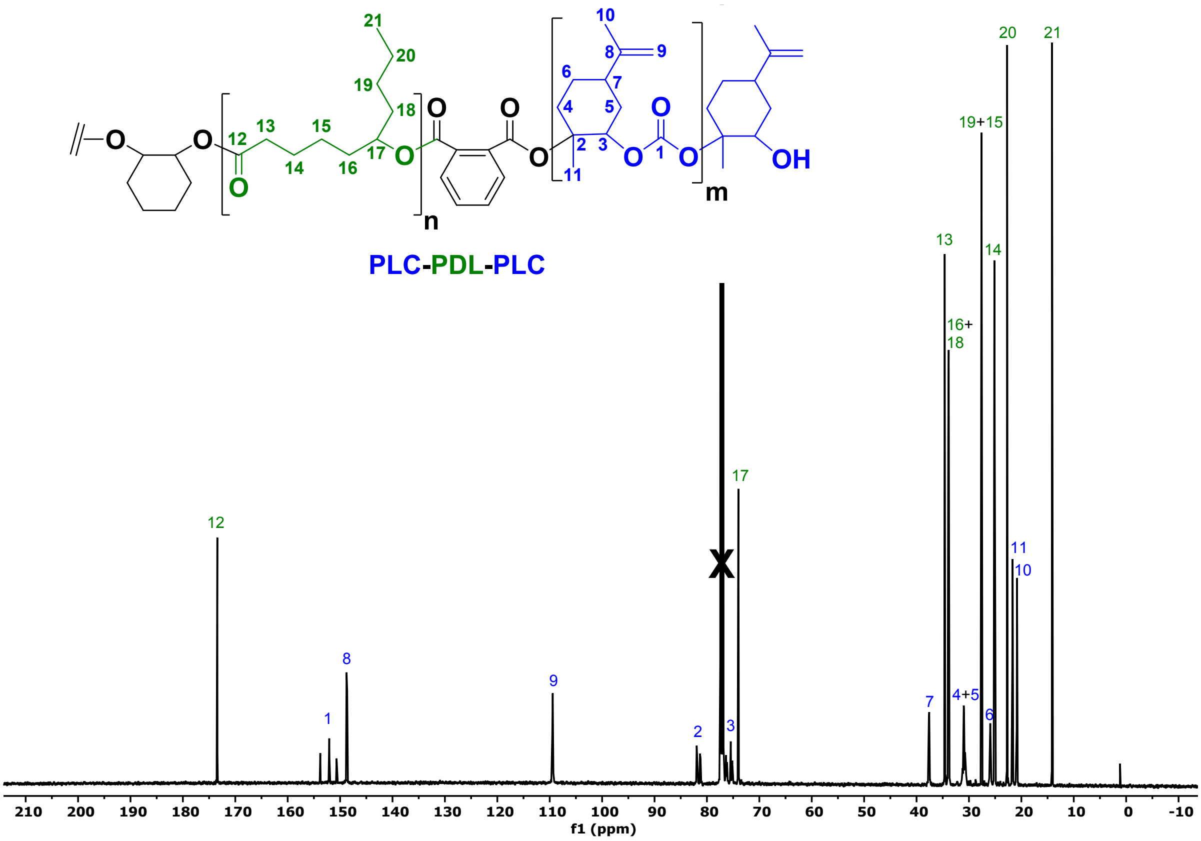


**Fig. S3** $^{13}$C{$^{1}$H}
ta NMR spectrum of PLC-*b*-PDL-*b*-PLC (in CDCl$_3$).

## 5. Size Exclusion Chromatography (SEC) Data

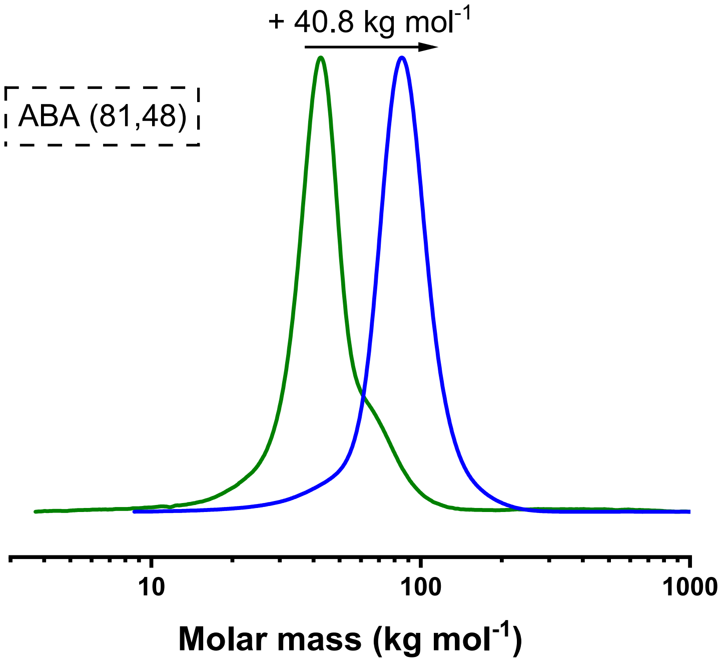


**Fig. S4** SEC traces acquired during the synthesis of ABA(81, 48). Green trace shows the PDL precursor and blue trace shows ABA(81, 48).

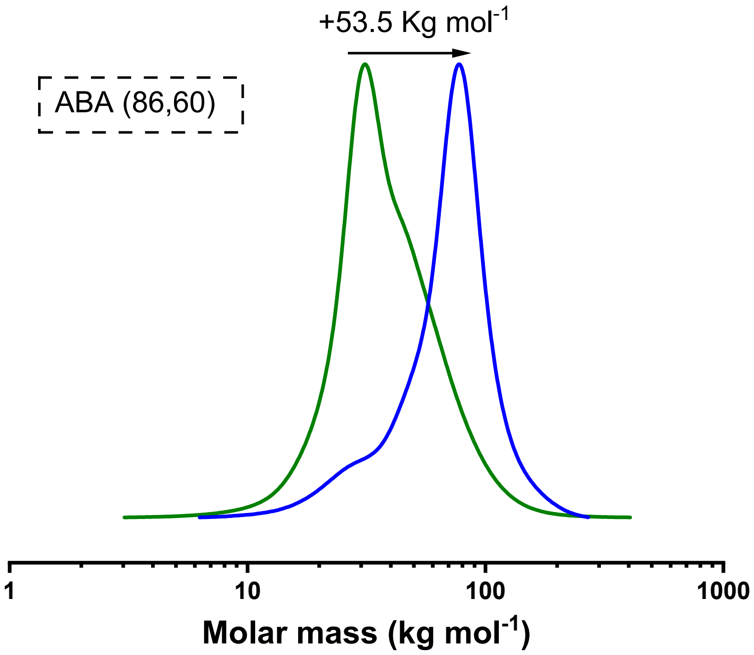


**Fig. S5** SEC traces acquired during the synthesis of ABA(86, 60). Green trace shows the PDL precursor and blue trace shows ABA (86,60).

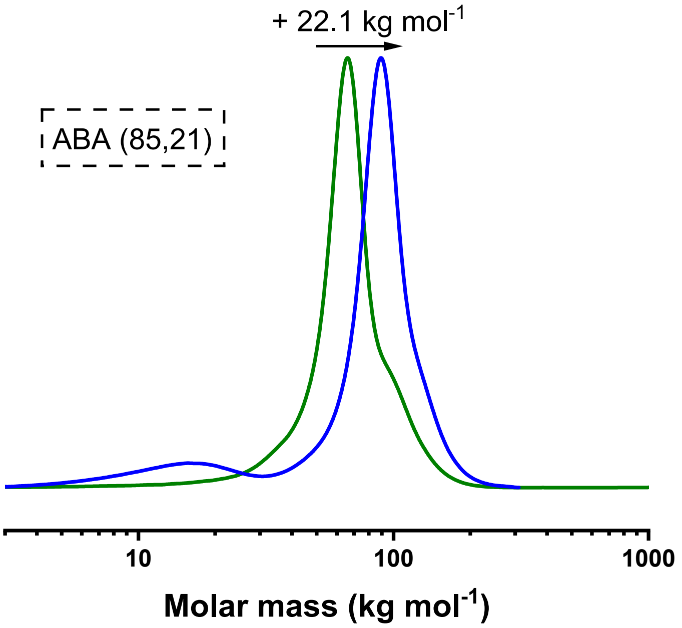


**Fig. S6** SEC traces acquired during the synthesis of ABA(85, 21). Green trace shows the PDL precursor and blue trace shows ABA(85,21).

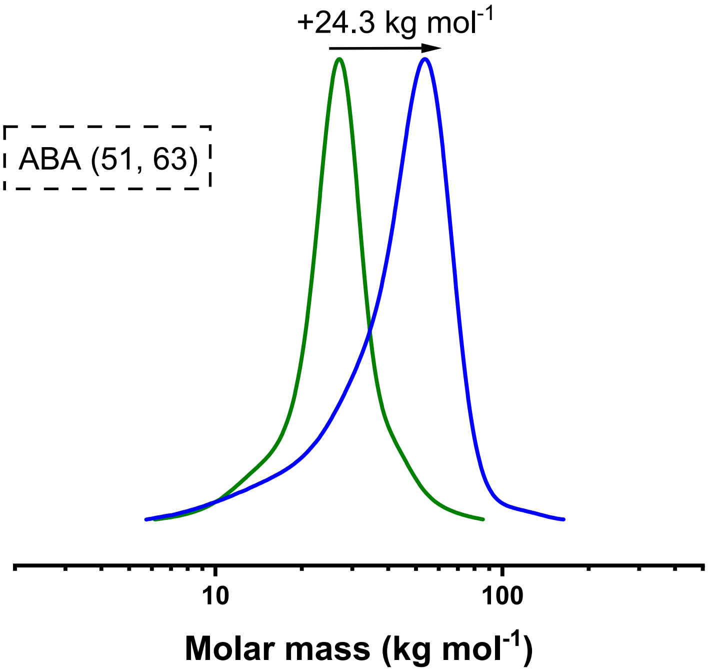


**Fig. S7** SEC traces acquired during the synthesis of ABA(51, 63). Green trace shows the PDL precursor and blue trace shows ABA(51,63).

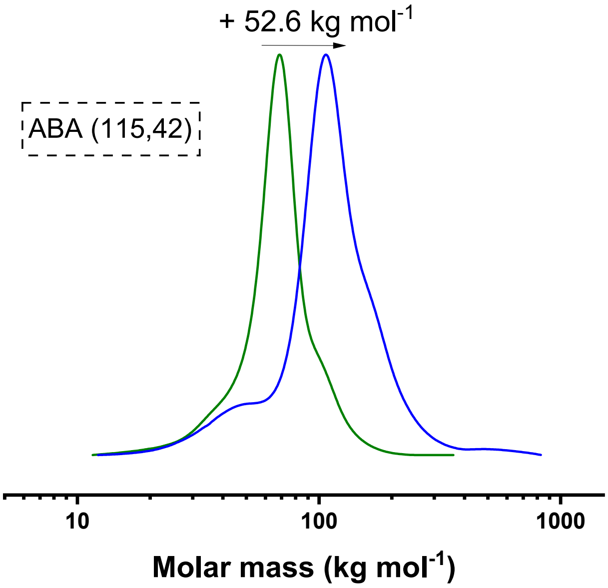
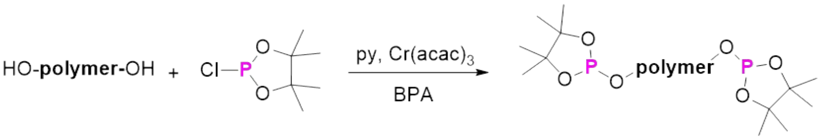


**Fig. S8** SEC traces acquired during the synthesis of ABA(115, 42). Green trace shows the PDL precursor and blue trace shows ABA(115,42).

## 6. Polymer Chain End-Group Analysis



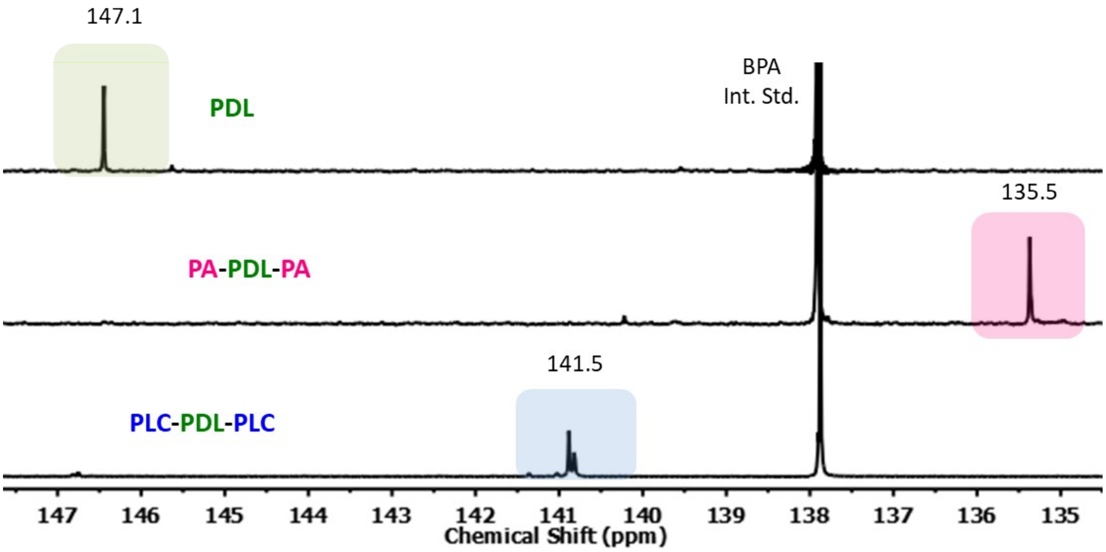


**Fig. S9** $^{31}P\{^1H\}$ NMR spectra used in end group analysis for the synthesis of PLC-PDL-PLC.

## 7. Differential Scanning Calorimetry (DSC) Data

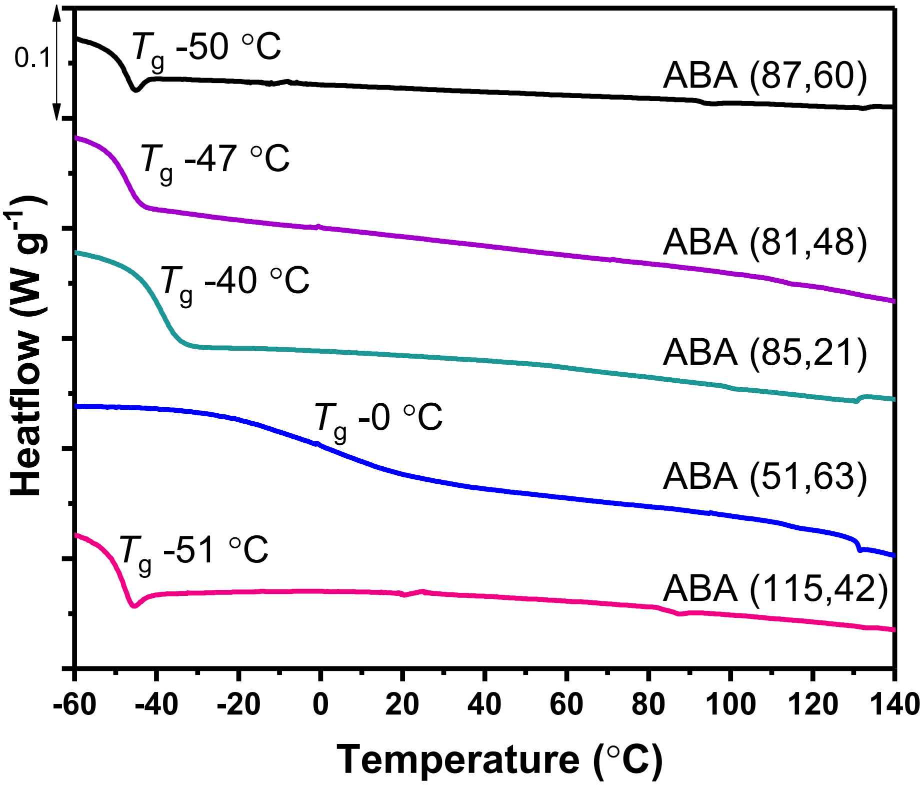


**Fig. S10.** DSC (second heating curve) of all triblock polymer samples, heated at a rate 10 °C min$^{-1}$.

## 8. Thermal Gravimetric Analysis (TGA) Data

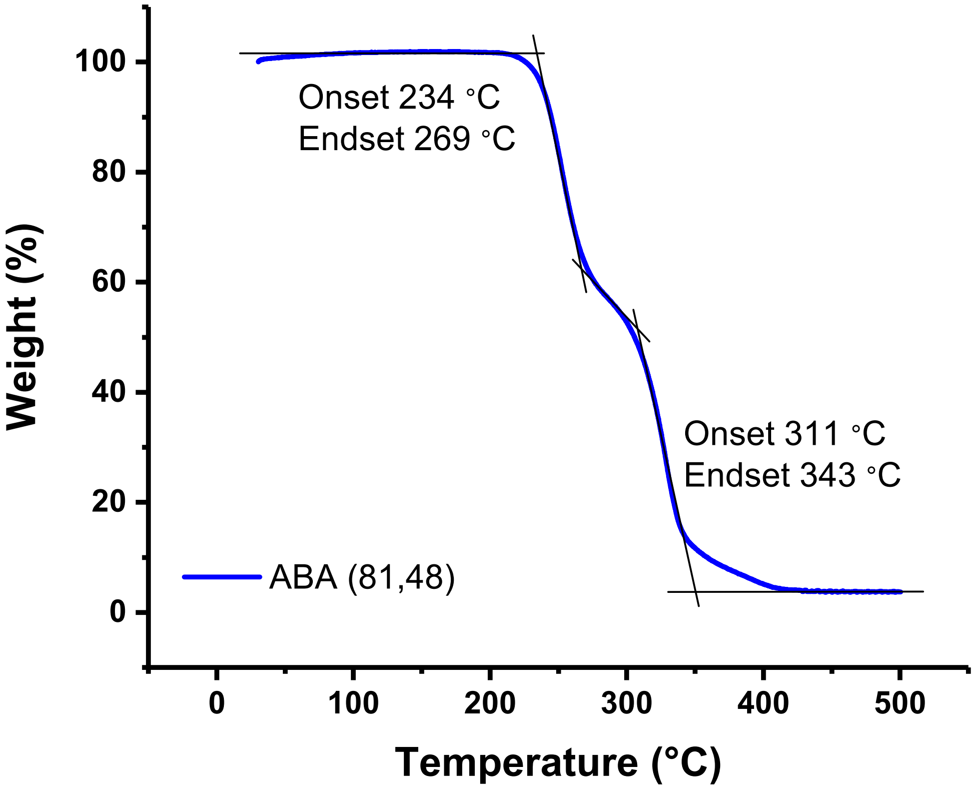


**Fig. S11** TGA data for ABA(81, 48).

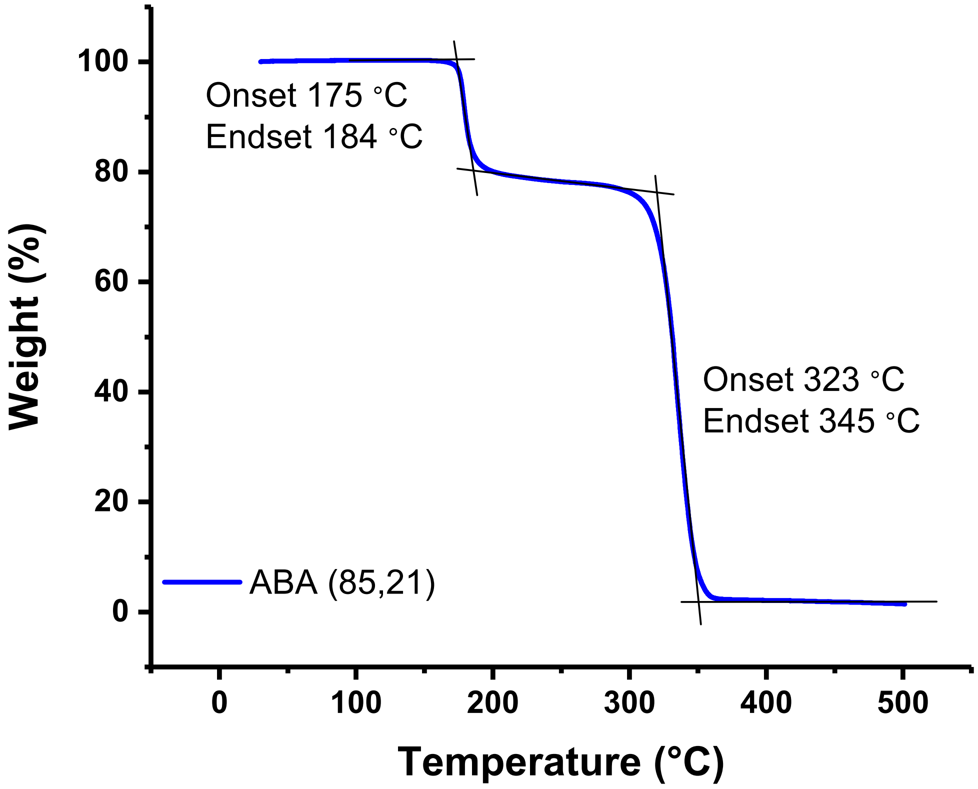


**Fig. S12** TGA data for ABA(85,21).

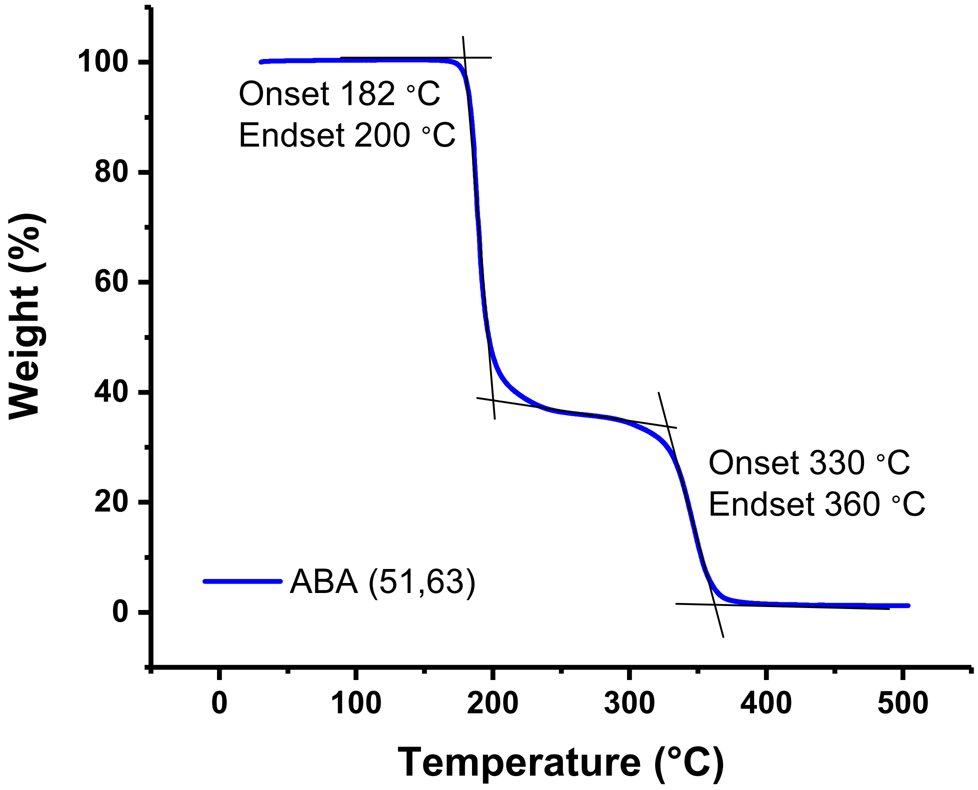


**Fig. S13** TGA data for ABA(51,63).

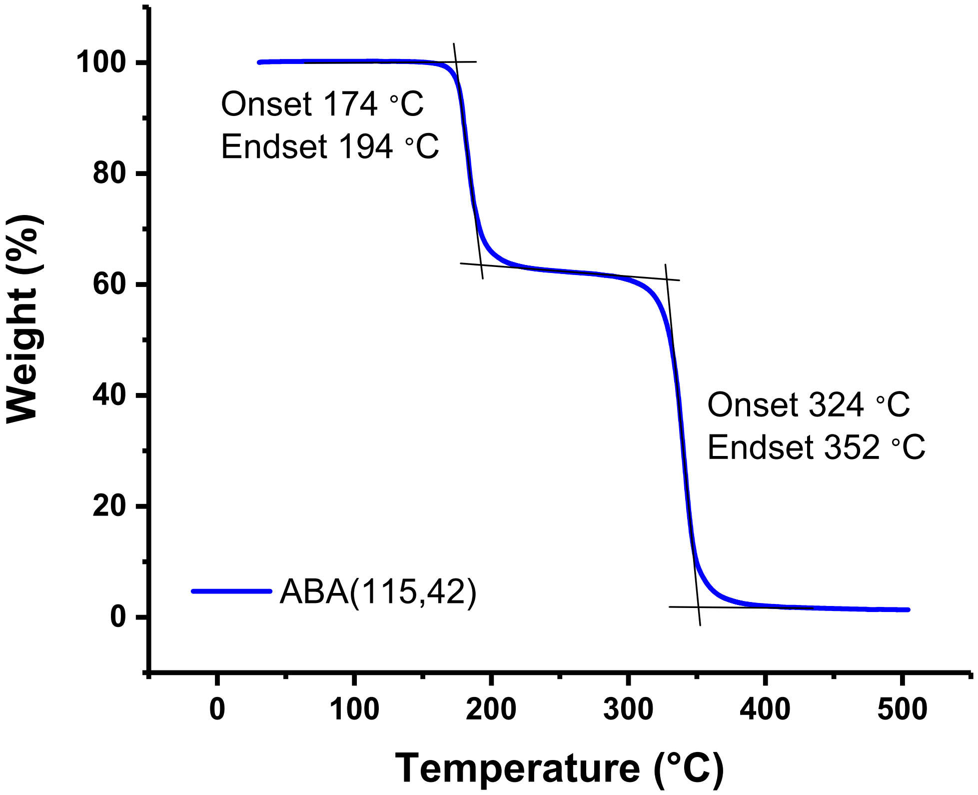


**Fig. S14** TGA data for ABA(115,42).

## 9. Mechanical Properties of the Block Polymers

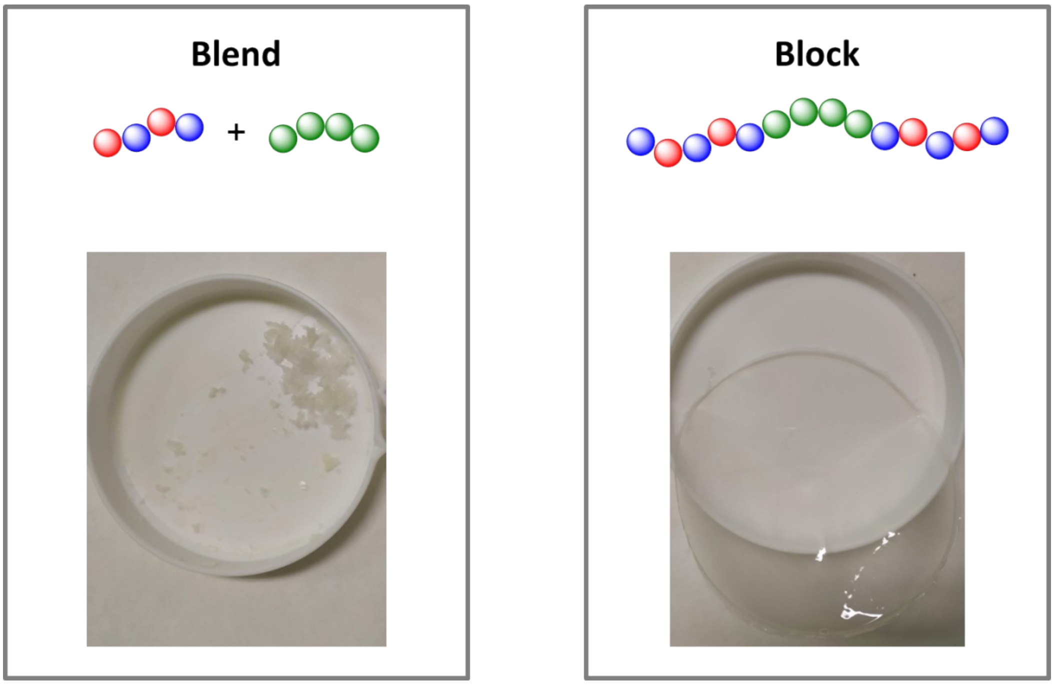


**Fig. S15** Digital photographs showing an attempt to solvent cast a blend of PLC and PDL (LHS) and a successful solvent cast of PLC-*b*-PDL-*b*-PLC (ABA (87,60)) forming a freestanding film (RHS).

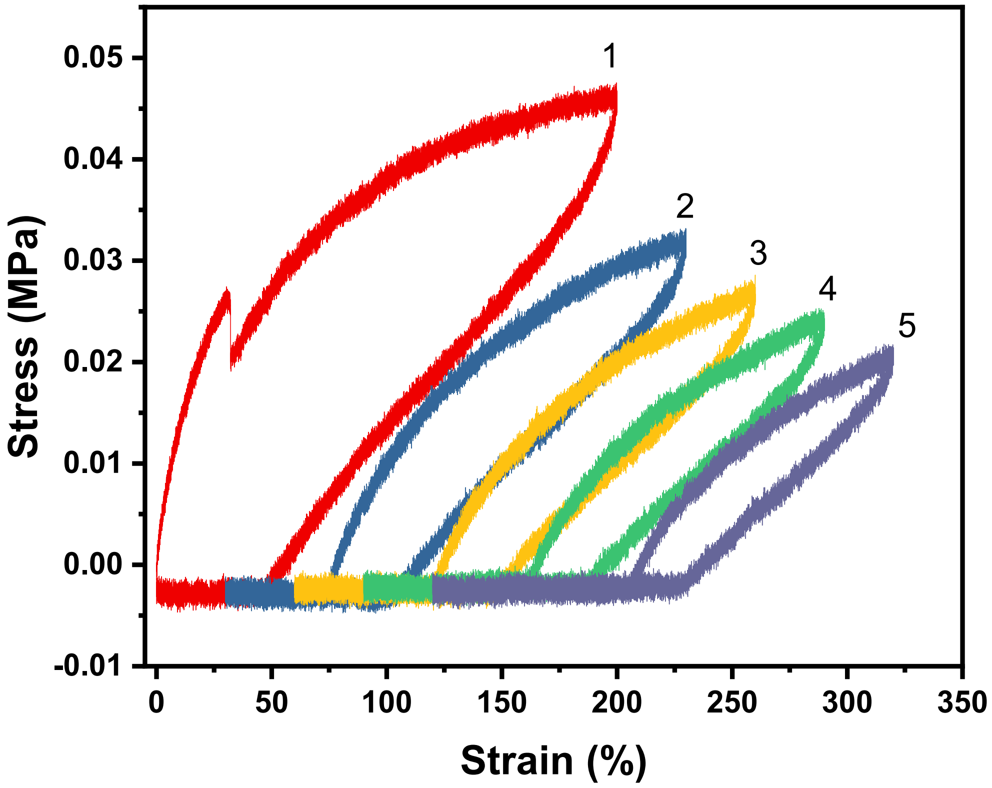


**Fig. S16** Cyclical tensile testing for ABA (81,48) (0-200 % strain, 10 cycles). Curves 1 -5 shown with a horizontal offset for clarity.

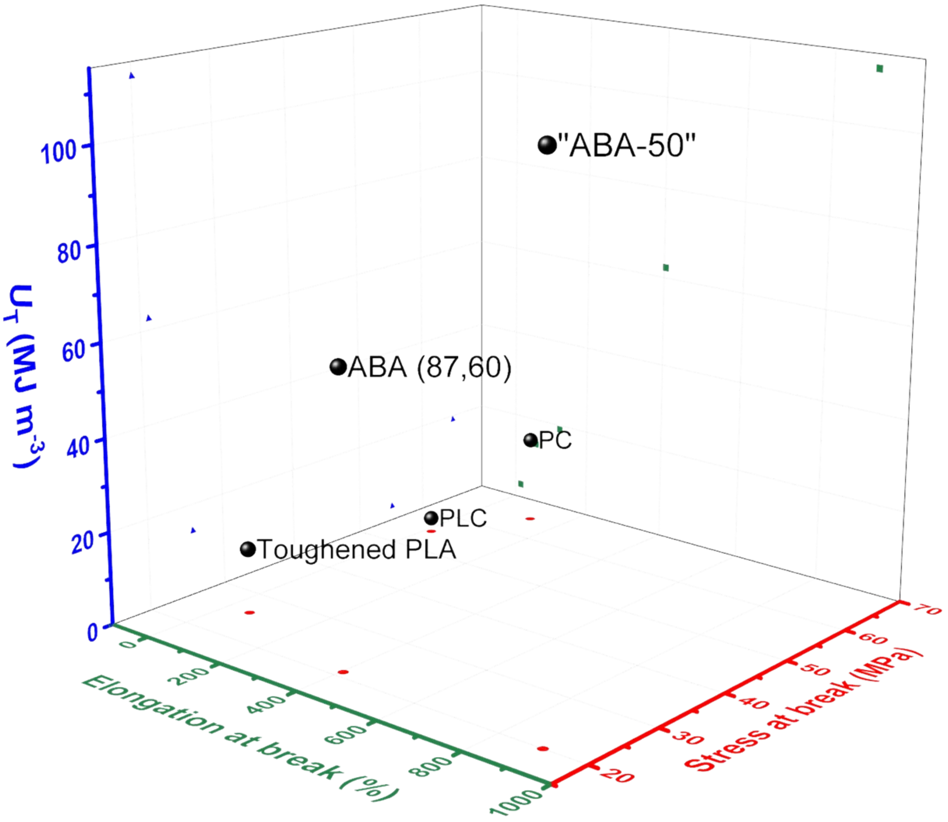


**Fig. S17** 3D scatter plot comparison of mechanical properties of ABA (87,60) and selected commercial and literature materials. Tensile toughness ($U_T$) = blue axis (zy plane) & triangle marker; elongation at break ($\varepsilon_b$) = green axis (xz plane) & square marker; stress at break ($\sigma_b$) = red axis (xy plane) & circle marker.

**Table S1. Mechanical Properties of ABA (87,60) and Selected Commercial and Literature Comparisons.**

| Material | Elongation at break (%) | Stress at break (MPa) | Tensile toughness (MJ m$^{-3}$) | Ref. |
|---|---|---|---|---|
| ABA (87,60) | 404 | 21 | 62.3 | This work |
| PC | 125 | 65 | 19.0 | [6] |
| PLC | 15 | 55 | 3.15 | [6] |
| Toughened PLA | 58 | 26 | 14 | [7] |
| ABA-50 | 900 | 20 | 112 | [8] |
| PLC-*b*-PHB (low MW) | 4 | 44 | *n.d.* | [9] |
| PLC-*b*-PHB (high MW) | 18 | 38 | *n.d.* | |

## 10. Depolymerization Experiments and Data

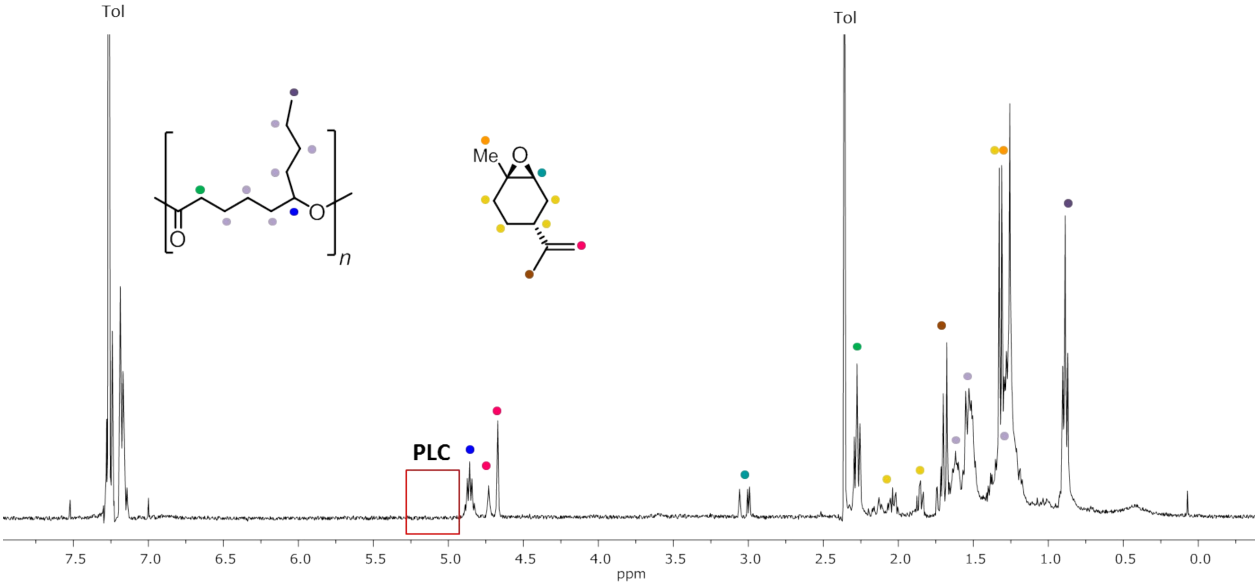


**Fig. S18** $^1$H NMR spectrum ($CDCl_3$) of aliquot from the depolymerization of ABA (87,60), using catalyst **1** in toluene, at 80 °C. Complete depolymerization of the PLC blocks is indicated by the absence of PLC signals (red square). Assignment of LO product peaks, alongside remaining PDL environments are shown. Tol = toluene solvent peaks.

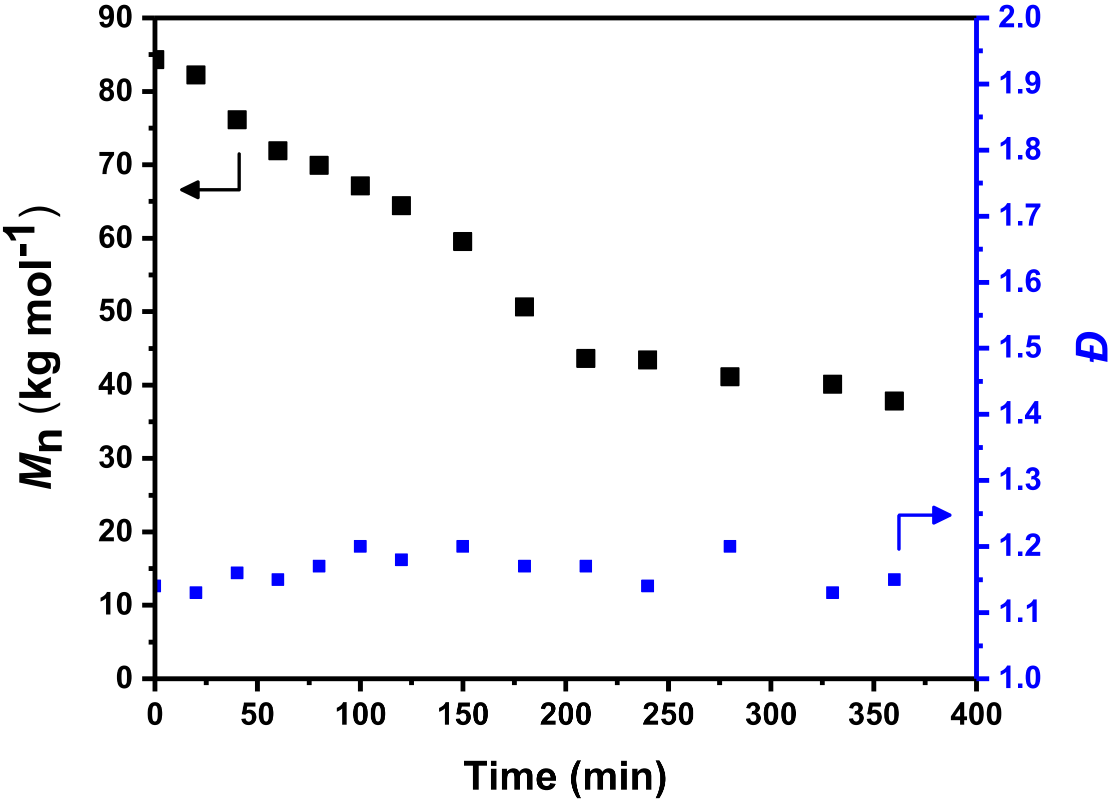


**Fig. S19** Depolymerization data showing evaluation of molar mass and dispersity against time for ABA (87,60). Aliquots taken at various time-points were analysed by SEC (THF eluent, vs. PS standards).

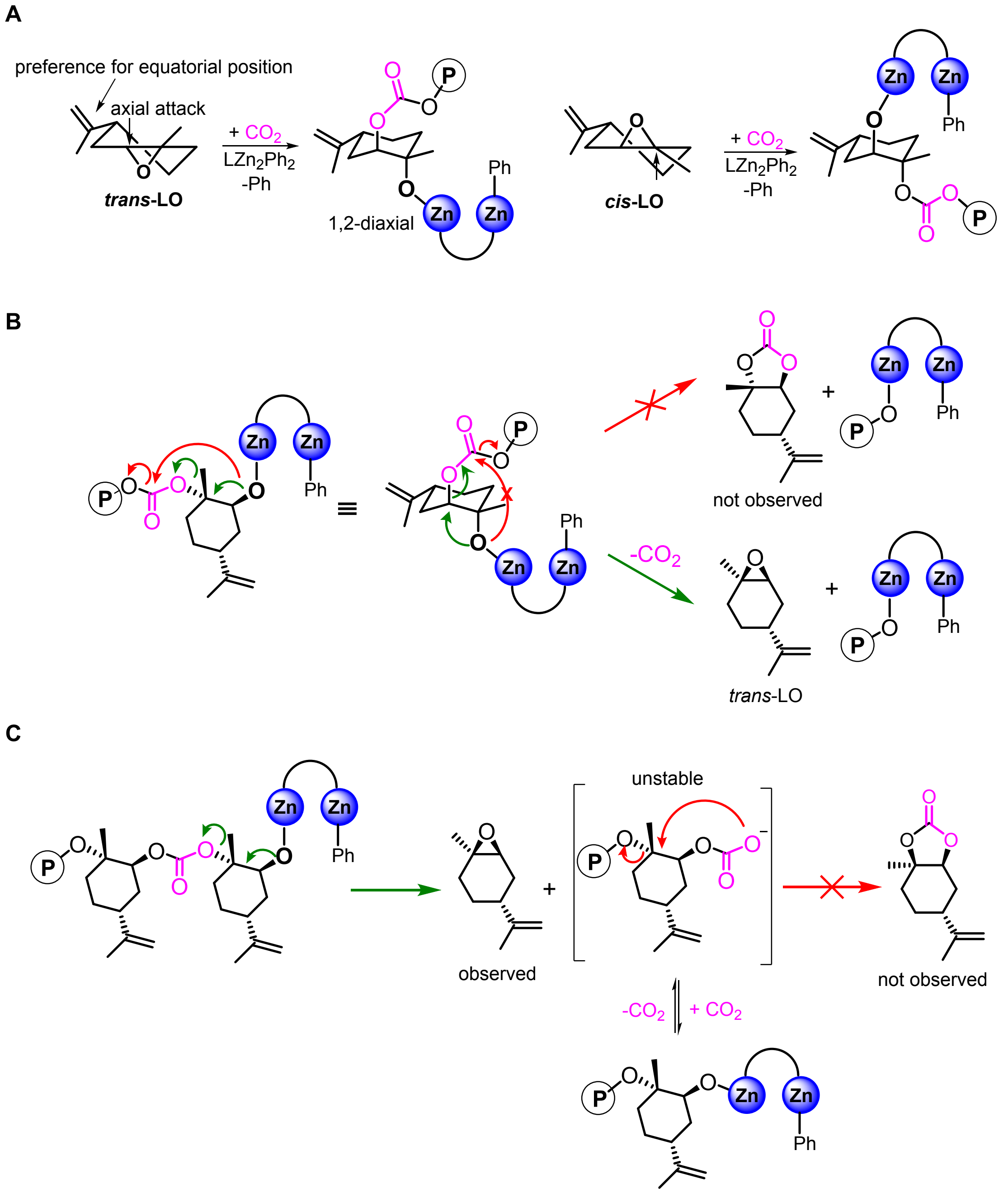


**Fig. S20** Proposed reactions occurring during depolymerization of PLC to LO, modified from Koning and coworkers.[10] **A:** Epoxide ring-opening to preferentially yield zinc-alkoxide and polymer chain in 1,2-diaxial position. Preference for the bulky isopropenyl group to occupy an equatorial position has been supported computationally and effectively locks the ring structure.[11] Preferential axial attack at the epoxide leads to a di-axial ring-opened product regardless of whether *cis*- or *trans*-LO.[12] **B**: Back-biting of polymer chain-end to form the epoxide. The alkoxide is unable to attack at the carbonyl carbon and form the trans- 5-membered cyclic carbonate. NB. Mechanism only illustrated for trans-LO. **C:** Backbiting of the carbonate end-group generated on formation of trans-LO to form the cis-cyclic carbonate product. This is based on the computational study presented by Darensbourg et al. for poly(cyclo pentene carbonate) depolymerization.[13] It is thought rapid decarboxylation prevents formation of the cis-cyclic carbonate by-product.

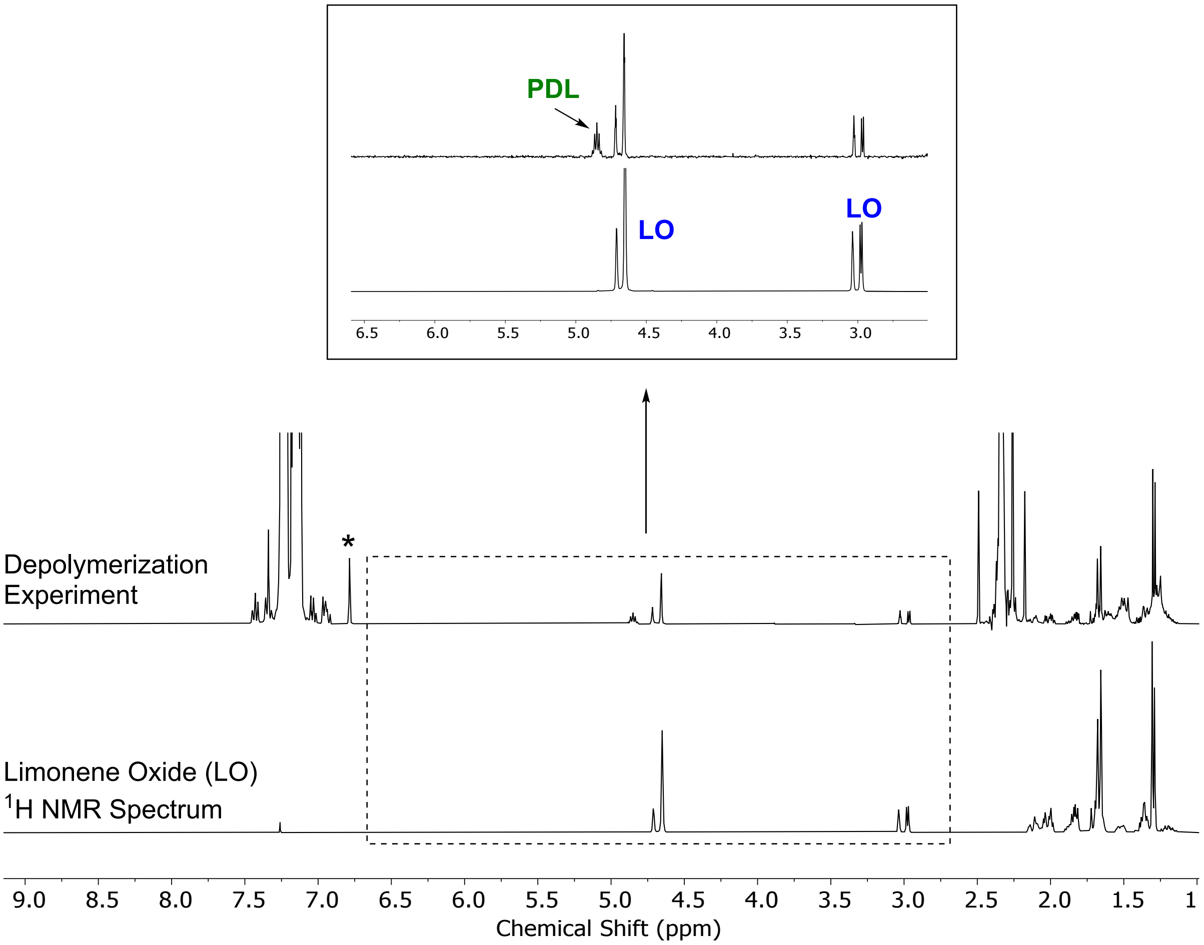


**Figure S21.** $^1$H NMR spectrum comparison between final aliquot from depolymerisation experiment (performed in toluene) and limonene oxide (* = mesitylene used as internal standard). Insert: selected region of interest shows presence LO and PDL only. The integrals of these correspond to the expected block ratio (PDL:LO = 40:60) and suggest no further degradation of the LO has occurred during the depolymerisation.

## 11. Degradation of PDL

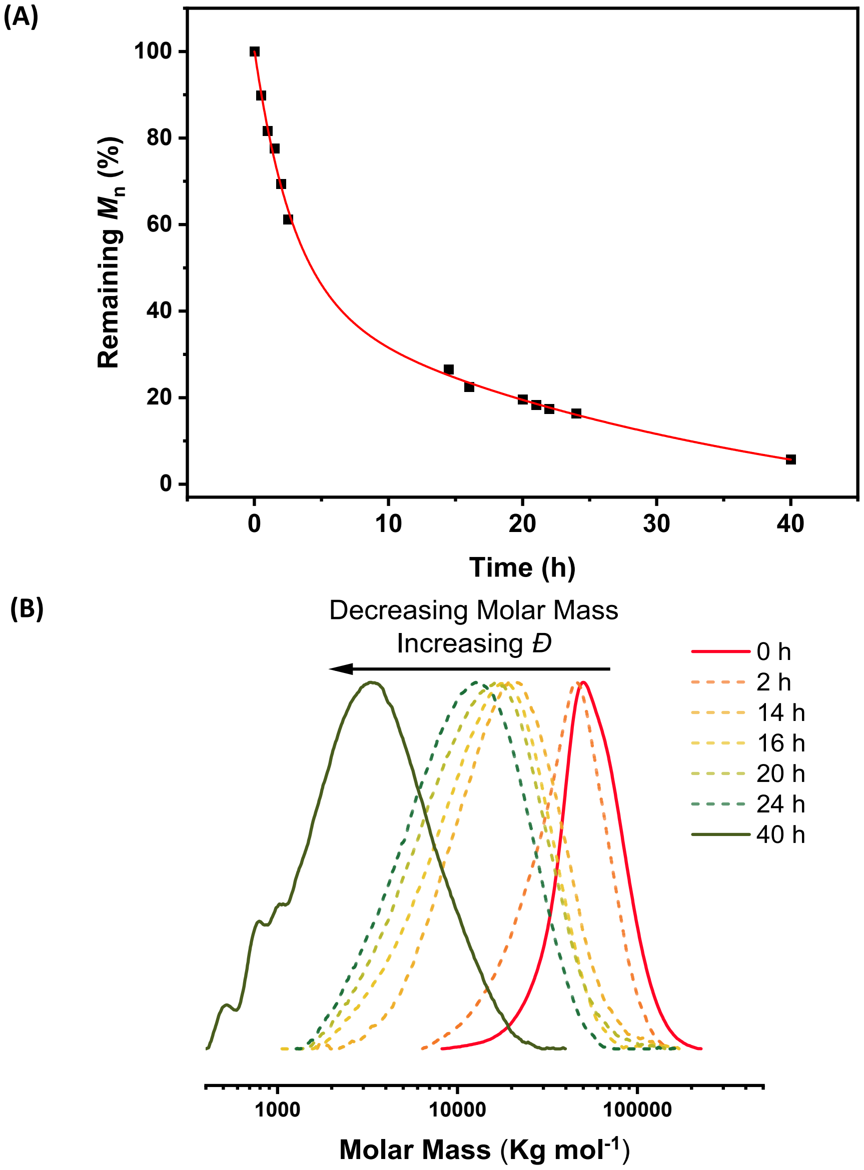


**Figure S22**. Degradation of PDL. Reaction conducted in THF with *p*-toluenesulfonic acid (0.01 M) at 60 ºC: (A) Remaining $M_n$ *vs.* Time profile (B) Stacked SEC traces showing a constant decrease in molar mass and increase in *Đ*.

## 12. References

1. M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931-933.
2. Y. Zhu, C. Romain and C. K. Williams, *J. Am. Chem. Soc.*, 2015, **137**, 12179-12182.
3. L. P. Carrodeguas, J. Gonzalez-Fabra, F. Castro-Gomez, C. Bo and A. W. Kleij, *Chem. - Eur. J.*, 2015, **21**, 6115-6122.
4. A. Schulz and A. Villinger, *Chem. - Eur. J.*, 2015, **21**, 3649-3663.
5. A. Spyros, D. S. Argyropoulos and R. H. Marchessault, *Macromolecules*, 1997, **30**, 327-329.
6. O. Hauenstein, S. Agarwal and A. Greiner, *Nat. Commun.*, 2016, **7**.
7. P. A. Delgado and M. A. Hillmyer, *RSC Adv.*, 2014, **4**, 13266-13273.
8. G. S. Sulley, G. L. Gregory, T. T. D. Chen, L. Peña Carrodeguas, G. Trott, A. Santmarti, K.-Y. Lee, N. J. Terrill and C. K. Williams, *J. Am. Chem. Soc.*, 2020, **142**, 4367-4378.
9. S. Kernbichl, M. Reiter, J. Mock and B. Rieger, *Macromolecules*, 2019, **52**, 8476-8483.
10. C. L. Li, R. J. Sablong, R. A. T. M. van Benthem and C. E. Koning, *ACS Macro Lett.*, 2017, **6**, 684-688.
11. F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo and G. W. Coates, *Macromolecules*, 2015, **48**, 2534-2550.
12. C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404-11405.
13. D. J. Darensbourg, S.-H. Wei, A. D. Yeung and W. C. Ellis, *Macromolecules*, 2013, **46**, 5850-5855.