

Supporting Information

Thermal, structural and degradation properties of an aromatic-aliphatic polyester built through ring-opening polymerisation

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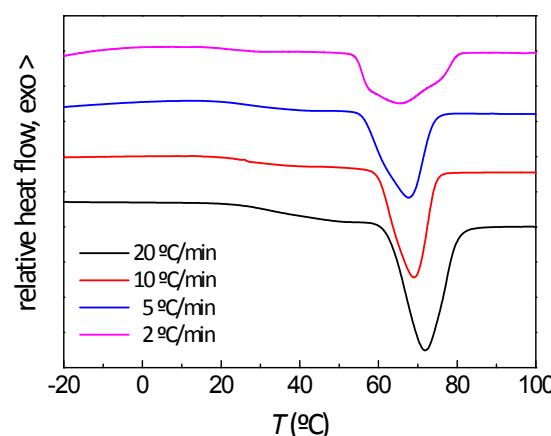


Fig. S1. DSC 1st heating traces of P2HEB obtained at different rates.

| Target M_n ^b (gmol ⁻¹) | Temperature (°C) | Solvent | Time (hr) | Conversion (%) ^a | M_n ^a (gmol ⁻¹) | \overline{D} ^c |
|--|---------------------|---------|--------------|--------------------------------|---|-----------------------------|
| 11,000 ¹ | 60 | Toluene | 6 | 99 | 11,600 | 1.14 |
| 40,000 ² | 60 | Toluene | 6 | 93 | 40,300 | 1.23 |
| 80,000 ³ | 60 | Toluene | 6 | 95 | 78,600 | 1.2 |

Table S1. Homopolymerisation of 2,3-DHB with $[2,3\text{-DHB}]_0:[\text{Al}]_0:[\text{BnOH}]_0 = {}^1 170:1:1$, ${}^2 2500:1:1$, ${}^3 1000:1:1$. ^aDetermined by ¹H NMR spectroscopy, ^b $M_{n,\text{th}} = ([2,3\text{-DHB}]/[\text{BnOH}]) \times \% \text{ conversion} \times MW\text{2,3-DHB}$, ^cDetermined by gel permeation chromatography versus polystyrene standards

| Heating rate | T_g (°C) | T_m (°C) | ΔH_m (J/g) |
|--------------|------------|------------|--------------------|
| 20 °C/min | 32.2 | 71.6 | 31.1 |
| 10 °C/min | 26.5 | 68.8 | 29.8 |
| 5 °C/min | 26.1 | 67.6 | 28.6 |
| 2 °C/min | 24.3 | 65.5 | 29.1 |

Table S2. Main thermal parameters extracted from 1st DSC heating scans depending on the heating rate.

| | M_n (g/mol) | M_w (g/mol) | P.I. |
|---------------|---------------|---------------|--------|
| Raw polymer | 6915 | 12119 | 1,7526 |
| After melting | 6873 | 12484 | 1,8163 |

Table S3. Gel permeation chromatography (GPC) results before and after heating.

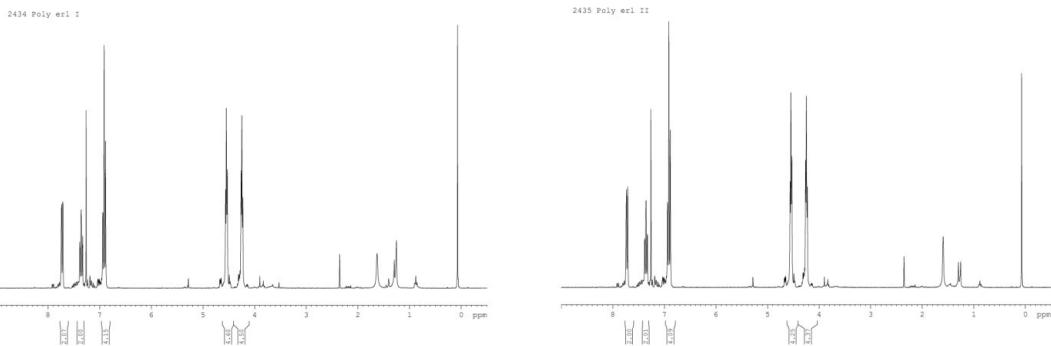


Fig. S2. ^1H NMR spectrum of P2HEB before (left) and after (right) melting.

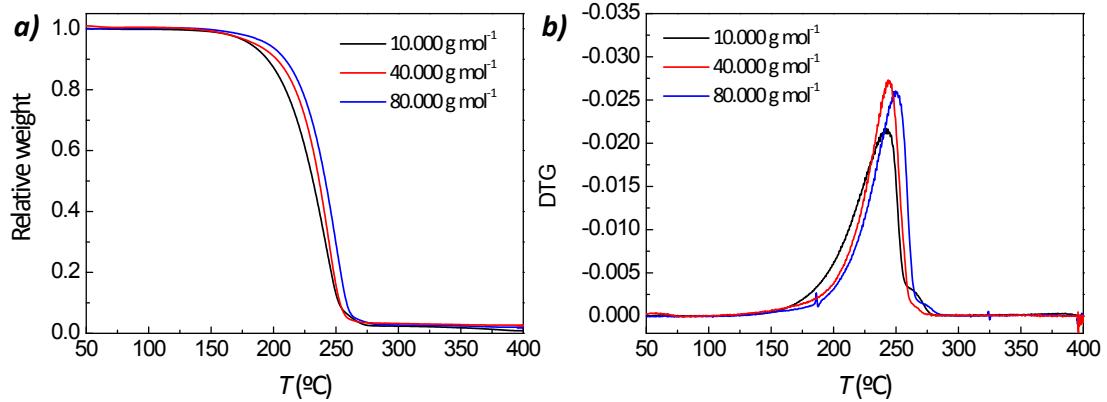


Fig. S3. Thermogravimetric traces (a) and weight lost rates (b) obtained at different heating rates under N_2 atmosphere for P2HEB having three different molecular weights.



Fig. S4. P2HEB solubility in different solvents has been evaluated. From left to right: hexane, toluene, chloroform, tetrahydrofuran (THF), cyclohexane and dimethylformamide (DMF). Best solvents are chloroform and DMF.

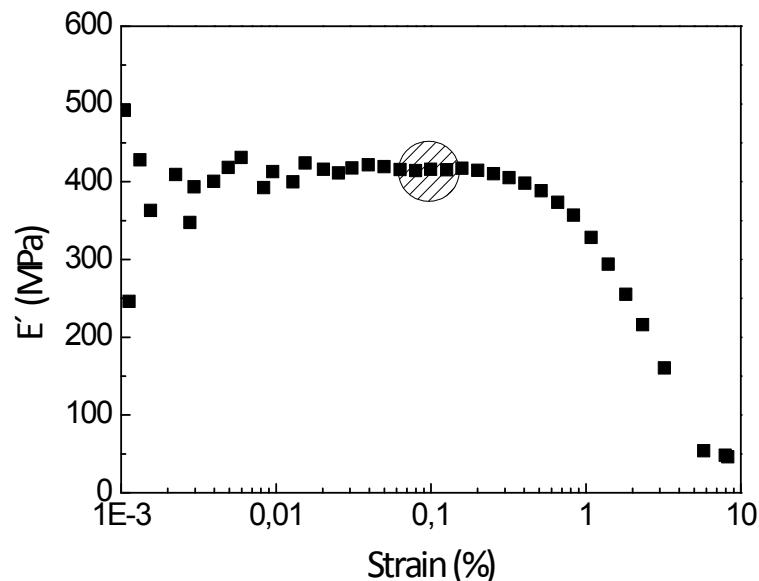


Fig. S5. Dynamic mechanical storage modulus (E') vs. strain for P2HEB having 80.000 g mol⁻¹. The inset shows the strain range in which DMA experiments have been carried out.

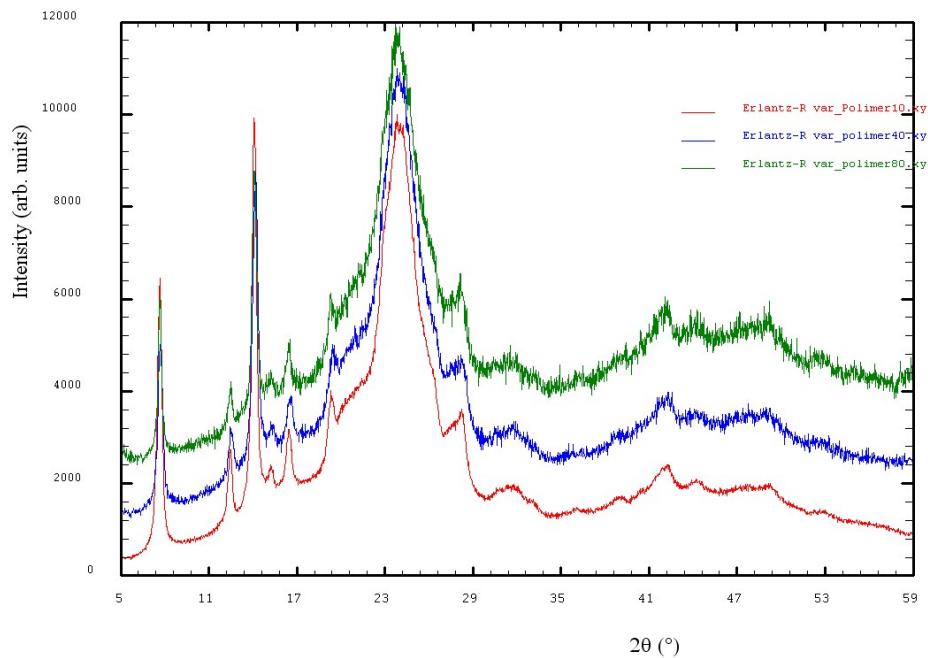


Fig. S6. Wide angle X-ray diffraction patterns of P2HEB having three different molecular weights ($10.000, 40.000$ and $80.000 \text{ g mol}^{-1}$).

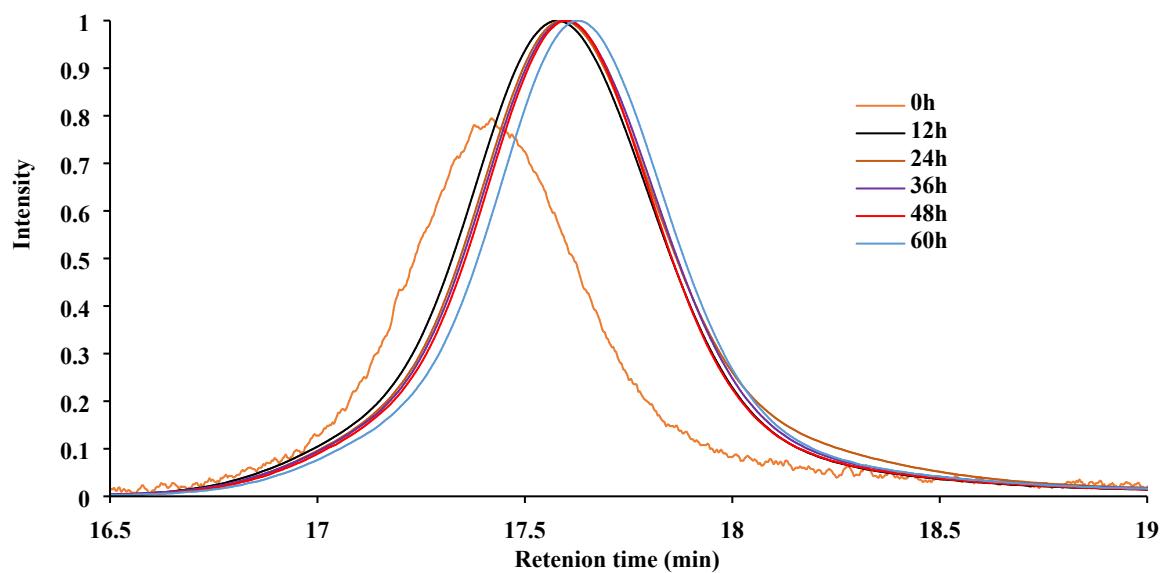


Fig. S7. GPC trace of P2HEB of molecular weight $78,600 \text{ gmol}^{-1}$ with their dispersity at 12-hour intervals to show the decrease in molecular weight as the degradation studies proceed.

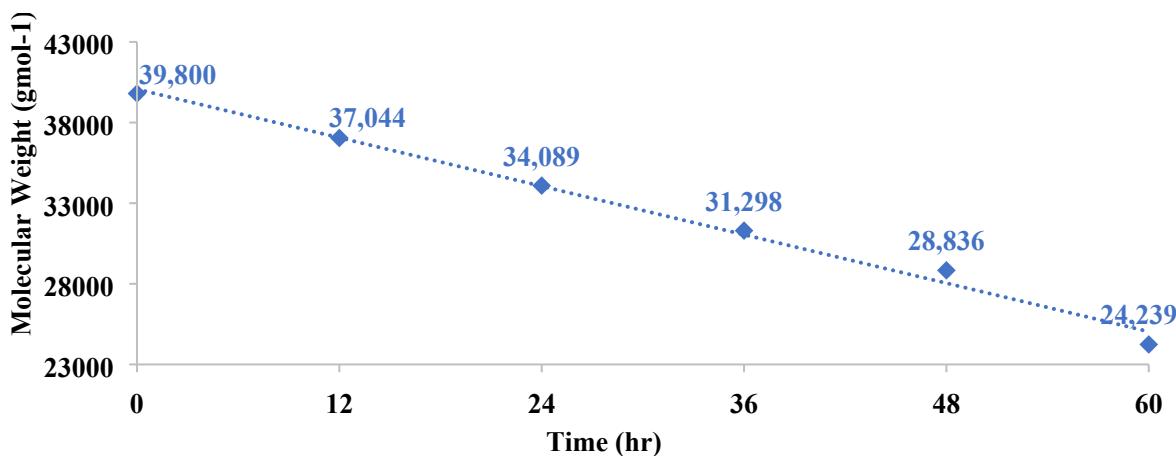


Fig. S8. Molecular weight determined by ^1H NMR at 12 hour intervals during enzymatic degradation of P2HEB of molecular weight 40,000 gmol⁻¹

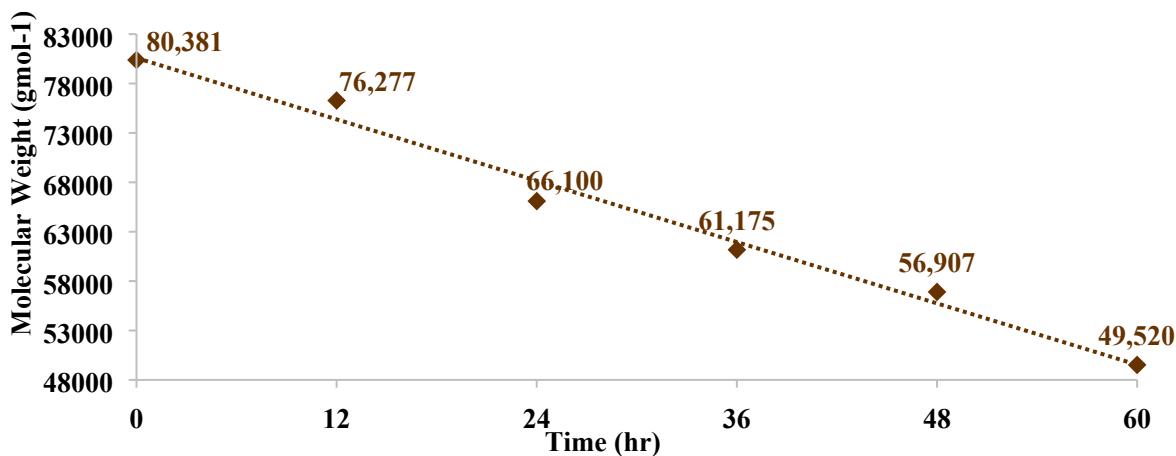


Fig. S9. Molecular weight determined by ^1H NMR at 12 hour intervals during enzymatic degradation of P2HEB of molecular weight 80,000 gmol⁻¹

| Time (hr) | M _n (gmol ⁻¹) | D |
|-----------|--------------------------------------|------|
| 0 | 40,300 | 1.23 |
| 12 | 39,400 | 1.26 |
| 24 | 39,000 | 1.25 |
| 36 | 38,600 | 1.23 |
| 48 | 37,500 | 1.26 |
| 60 | 36,100 | 1.27 |

Table. S4. P2HEB of molecular weight 40,300 gmol⁻¹ determined by gel permeation chromatography, dn/dc value used to calculate M_n was 0.115, D=dispersity=M_w/M_n.

| Time (hr) | M _n (gmol ⁻¹) | D |
|-----------|--------------------------------------|------|
| 0 | 78,600 | 1.22 |
| 12 | 76,800 | 1.23 |
| 24 | 74,400 | 1.24 |
| 36 | 73,200 | 1.23 |
| 48 | 72,500 | 1.25 |
| 60 | 70,100 | 1.24 |

Table. S5. P2HEB of molecular weight 78,600 gmol⁻¹ determined by gel permeation chromatography, dn/dc value used to calculate M_n was 0.11, D=dispersity=M_w/M_n.