

Thermal, structural and degradation properties of an aromatic-aliphatic polyester built through ROP

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Introduction

> Increasing environmental impact of plastic waste from commodity plastics such as poly(ethylene terephthalate) (PET) has led to renewed interest in the life-cycle of polymeric materials.¹



✓ Exceptional thermal properties ($T_q = 67-81 \text{ °C}$)

- ✓ Low gas permeability
- ✓ High chemical resistance
- **×** Petroleum derived
- **×** Poorly (bio)degradable
- **×** Leaches phthalates

(E´)

> MacDonald et al. reported the ROP of a new monomer, 2,3-dihydro-5H-1,4-benzodioxepin-5-one (2,3-DHB), to afford the aromatic-aliphatic polyester poly(2-(2-hydroxyethoxy)benzoate) (P2HEB).² \geq P2HEB has its aromatic ring in the ortho position similar to the ortho-linked poly(ethylene phthalate) (PEP) (T_g = 38.2 °C).³

> Unlike PEP it is able to undergo selective depolymerisation back to its cyclic monomer under mild conditions by exploiting the monomer-polymer equilibrium using aluminium salen 1 as the catalyst.²



> We expand upon this research to target higher molecular weight P2HEB polymers to explore the effects of molecular weight on the polyester's thermal, mechanical and degradation behaviours.

Thermal Analysis

Differential Scanning Calorimetry:



 T_a slightly shifted toward higher temperatures with increase in molecular weight, while T_m showed a more obvious increase.



Mechanical and Structural Studies

Dynamic Mechanical Analysis:



Below T_{α} , P2HEB has a E' of 1050 MPa and behaves as a rigid body whereas above T_{a} , P2HEB behaves rubber like. The observed E' is around half of that of PLLA.^{7, 8}

Wide Angle X-ray Crystallography:

31000 -

Degradation Studies

Enzymatic Degradation:

Gel Permeation Chromatography (GPC) traces show a clear shift towards lower hydrodynamic volumes with addition of proteinase k in a Tris-HCI buffer of pH 8.6. This indicates a decrease, to the same extent, in molecular weight for both 40,000 (left) and 80,000 g mol⁻¹ (right) P2HEB polymer films.



The absence of the exothermic peak when P2HEB of 40,000 g mol⁻¹ is cooled down to 40 °C from the melt is due to it's poor crystallisation ability arising from the poor molecular mobility of longer chains.^{4, 5}

Thermogravimetric Analysis:



The thermal degradation in P2HEB occurs at an earlier temperature compared to poly (L-lactic acid) (PLLA), which at a heating rate of 10 °C/min, has an onset of thermal degradation at 290.5 °C.⁶



Đa	M _{n,th} (g mol⁻¹) ^b	M _n (g mol⁻¹) ^c
1.26	11,499	11,106
1.23	40,000	40,300
1.22	80,000	78,600

2,3-DHB:MeAI[salen]:BnOH = 70:1:1, 500:1:1, 1000:1:1, ^aDetermined by gel permeation chromatography. $D=dispersity=M_w/M_n$. $^bMn,th = [2,3-DHB]/[BnOH]) \times \%$ conversion $\times M_W$ 2,3-DHB. ^cDetermined by ¹H NMR spectroscopy

P2HEB shows a higher percentage weight loss than PET due to a higher degree of chain mobility, lower crystallinity and the ester linkages being susceptible to enzymatic attack.³ Conversely, the percentage of enzymatic degradation of P2HEB is lower than for atactic PLA.⁹ The absence of an aromatic ring to restrict the ester linkages allows for PLA's higher degradation.





The properties of P2HEB suggest potential applications of the polymer as a component of polymer blends, for example to alter the thermal and mechanical properties of PLA. P2HEB-PLA block copolymers will be accessed through manipulating the monomer-polymer equilibrium of P2HEB.



> $T_a \approx 27 \circ C$

thermal

degradation

of

- $T_m = 70-80 \text{ °C}$
- Poor crystallisation ability Stiff mechanical behaviour
- Enzymatically and chemically degradable (independent of molecular weight)

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Degradation of P2HEB films of all three molecular weights was investigated in the presence of the Lewis acid catalyst, aluminium salen 1.

The degree of degradation selectively back to its monomer after one hour is independent of molecular weight, with 80% molecular weight loss for each sample.

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Green Materials Laboratory