

# Novel multiblock copolymers (MBCP) from the depolymerization of PET

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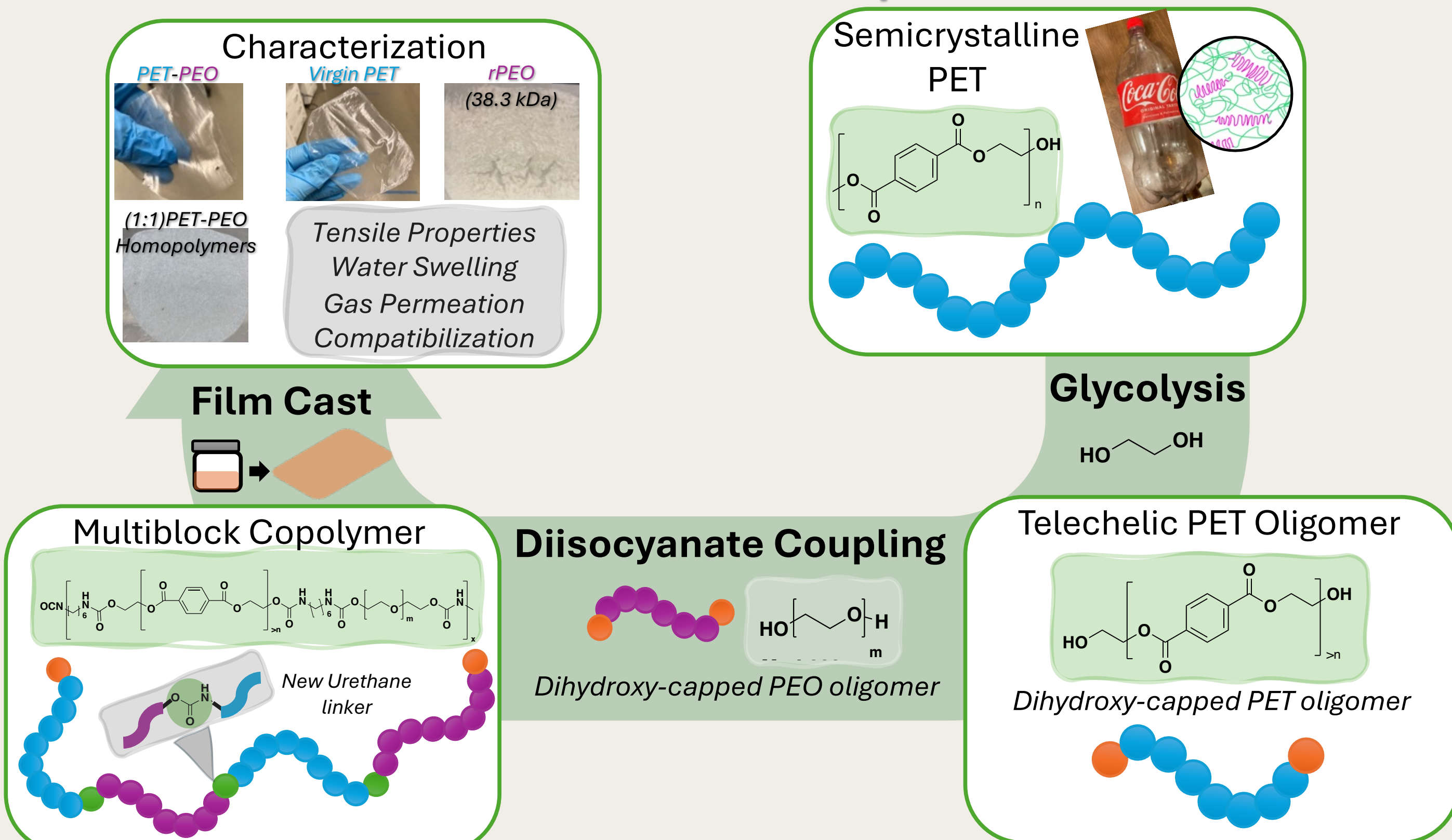
## Introduction

- Annually **400 million tons** of plastic are produced

- Only 9% recycled
- Chemical Recycling**
- Getting back to monomer is **energy and cost-intensive**

Can we tune properties obtained from upcycled materials?

How can we optimize chemical recycling of consumer waste to enhance repolymerization or create value-added products?



### Diisocyanate Coupling

- Efficient urethane formation
- Cross-linking and moisture-sensitive
- Good for hydroxyl-capped oligomers

### Goals of Research

Understand the depolymerization process to create feedstocks to repolymerize or synthesize value-added products

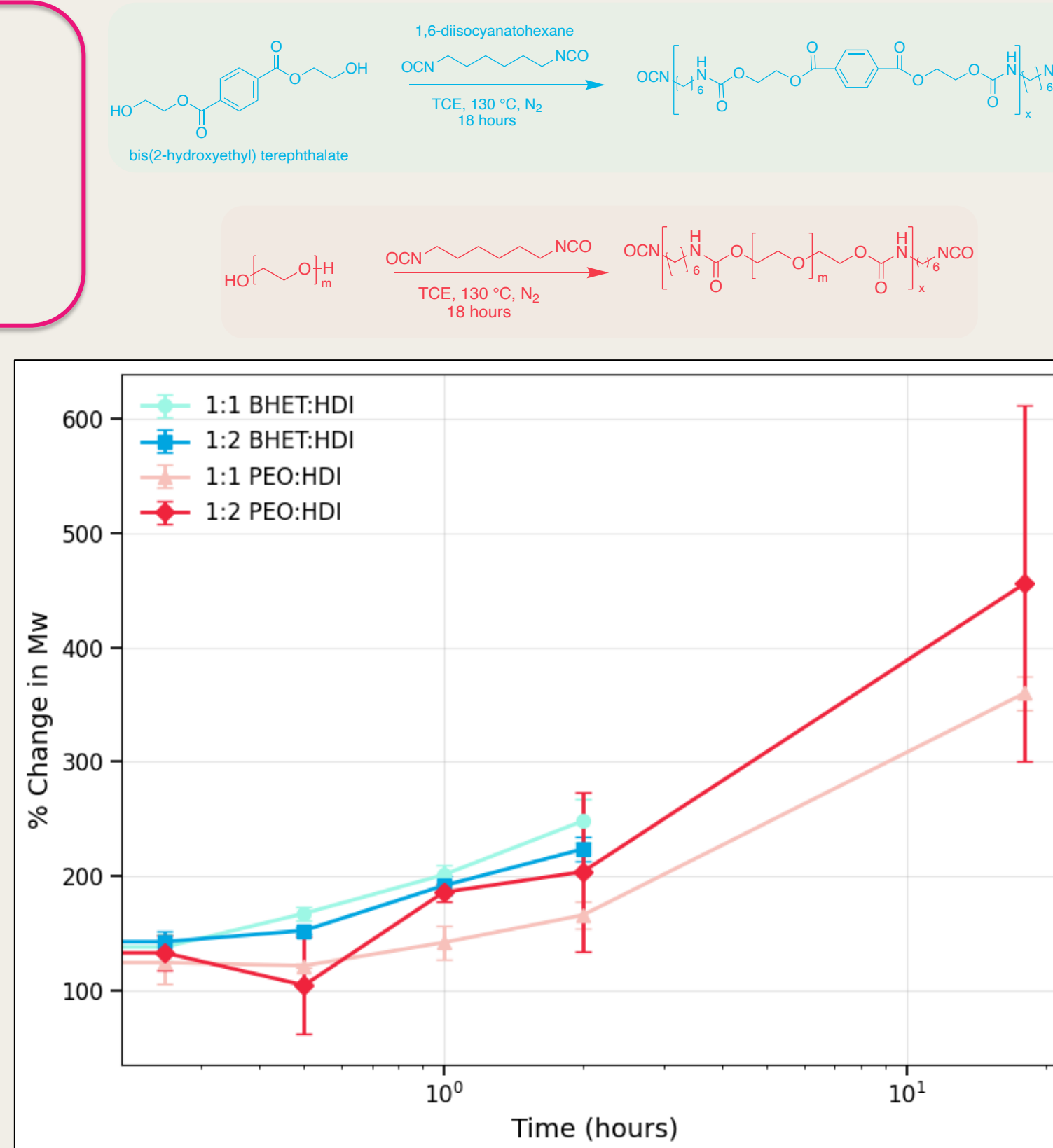
## Model System (BHET & PEO)

### Excess Diisocyanate

- 1:1 OH:NCO  $\rightarrow$  Step Growth
- 1:2 OH:NCO  $\rightarrow$  End-capping

- Even under “end-capping” conditions, the molecular weight keeps growing with time.
  - Urethane exchange, secondary reactions
- Long times promote oligomer-oligomer coupling, not just simple end-capping.

Short end-capping time limits oligomer coupling



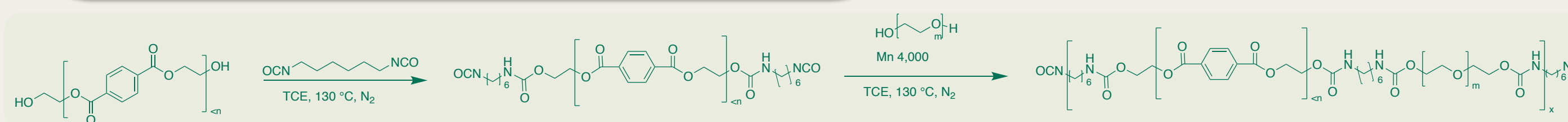
## PET-PEO MBCP Synthesis

### End-Capping Strategies

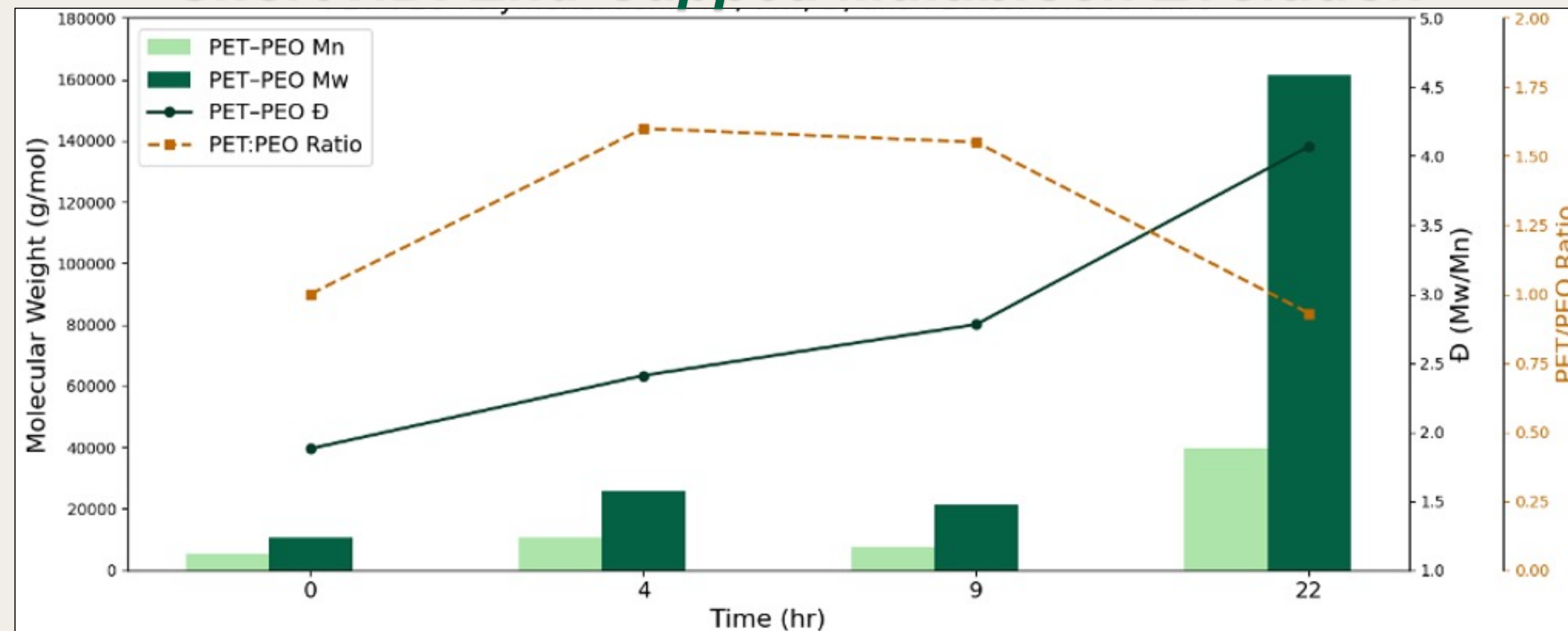
- Short HDI end-capping**
  - Add HDI to dPET for 10 minutes, then add PEO
- Long HDI end-capping**
  - Add HDI to dPET for 24 hours, then add PEO

### Feedstock

- dPET oligomers ( $M_n$  ~5.5-5.7 kg/mol, ~2 OH/chain)
- Dihydroxy-terminated PEO (4 kg/mol)



### Short HDI End-Capped Multiblock Evolution



### Controlling Architecture with End-Capping Time

#### Short end-capping

- Near 1:1 PET:PEO incorporation
- DOSY NMR has a single diffusion peak
- PET and PEO are covalently bonded

#### Long end-capping

- 1.67 PET blocks per 1.0 PEO block
- DOSY NMR has a single diffusion peak
- Significant PET-PET coupling before PEO is added.

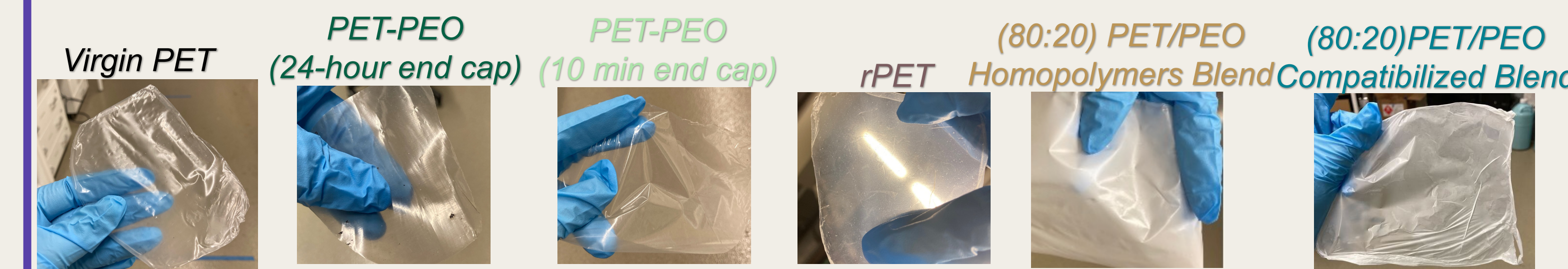
| End-capping Time (hours) | $M_n$ (kg/mol) | $M_w$ (kg/mol) | $\bar{D}$ | PET:PEO ratio |
|--------------------------|----------------|----------------|-----------|---------------|
| 0.167                    | 40             | 161            | 4.1       | 0.93          |
| 24.0                     | 29             | 108            | 3.8       | 1.67          |

End-capping time controls composition & connectivity

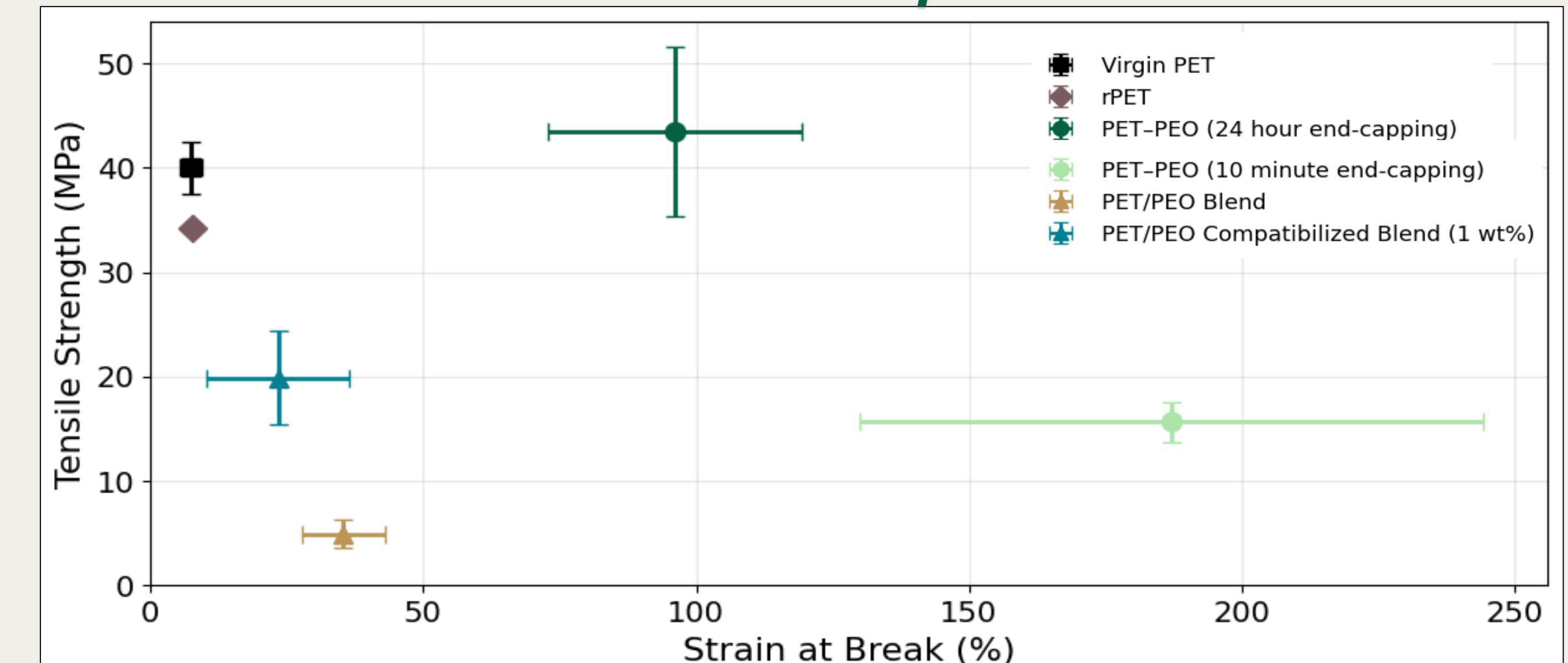
## Conclusion

- Telechelic PET oligomers from glycolysis can be upcycled into high-molecular-weight PET-PEO multiblock copolymers via HDI-mediated coupling.
- End-capping time controls composition and connectivity: short  $\rightarrow$  balanced PET-PEO multiblocks; long  $\rightarrow$  PET-enriched sequences
- Recycled PET-based MBCPs can approach commercial PEO-PBT membrane performance using waste-derived feedstocks.
- This HDI-mediated telechelic coupling can be extended to other recycled oligomers (PC, nylon, PET textiles, polyethylene-derived diols), offering a modular platform for upcycling mixed plastic waste.

## PET-PEO MBCP Properties



### Mechanical Properties



### PET-PEO MBCP

- 24 h end-capped** (PET-rich): similar strength to **Virgin PET** (~44 MPa), much higher ductility (>90% strain). Long PET + short PEO form hard domains bridged by flexible segments.
- 10 min end-capped** (more PEO): lower strength to **Virgin PET**, much higher ductility (>150% strain), making it tough and energy-absorbing.

### Blends vs MBCP

- 80:20 uncompatibilized PET/PEO**: poor integrity, phase separation.
- 1 wt% compatibilizer** improves but remains weaker than multiblocks.

### Gas Permeability & Membrane Performance

| Sample                                                | Permeability |                |                |                 |                 |                |
|-------------------------------------------------------|--------------|----------------|----------------|-----------------|-----------------|----------------|
|                                                       | He           | H <sub>2</sub> | N <sub>2</sub> | CH <sub>4</sub> | CO <sub>2</sub> | O <sub>2</sub> |
| PolyActive (4000PEO <sub>55</sub> PBT <sub>45</sub> ) | ---          | 10.55          | 2.61           | 6.76            | 112             | ---            |
| PolyActive (PEO-PBT/GO-0)                             | ---          | 14.3           | 2.88           | 8.4             | 150             | ---            |
| PET-PEO (10-min End-Capped)                           | 138.59       | 243.69         | 52.31          | 22.51           | 223.95          | 197.36         |

### Compatibilized Blends

- Higher CO<sub>2</sub> permeability than virgin PET but lower selectivity than **MBCPs** and **PolyActive**.

### PET-PEO MBCP

- CO<sub>2</sub> permeability comparable to **PolyActive**
- CO<sub>2</sub>/CH<sub>4</sub> selectivity is slightly below **PolyActive** but clearly superior to **blends**.

