Green strategies for efficient enzymatic degradation of plastic wastes

1st year PhD report

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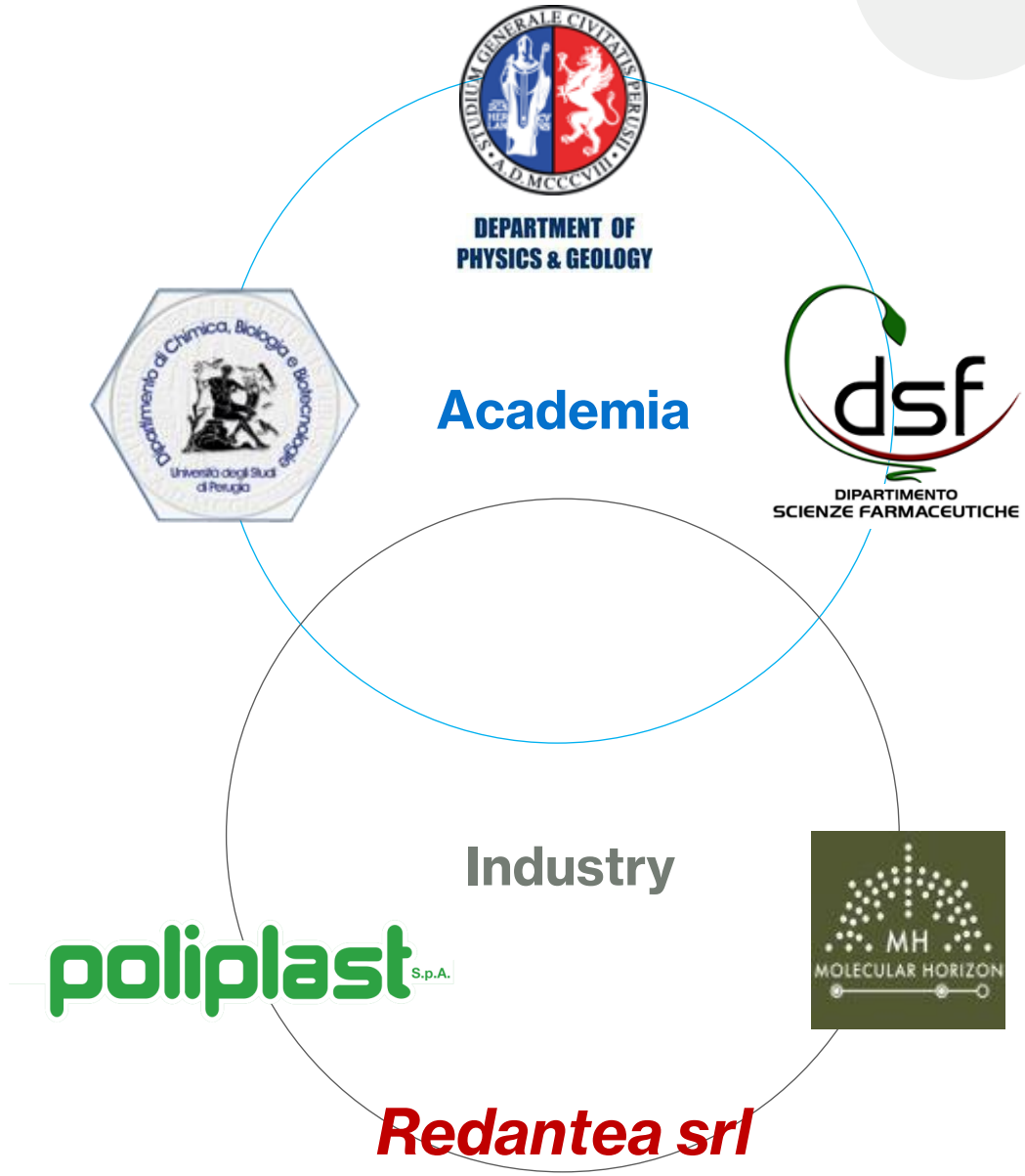
Tutor: Prof. Silvia Corezzi

28-10-2022

Few things about the project...

- **New line of research**, started with my PhD (PON funding)
- Required intensive **literature review**
- Very **interdisciplinary** nature, many collaborations needed!

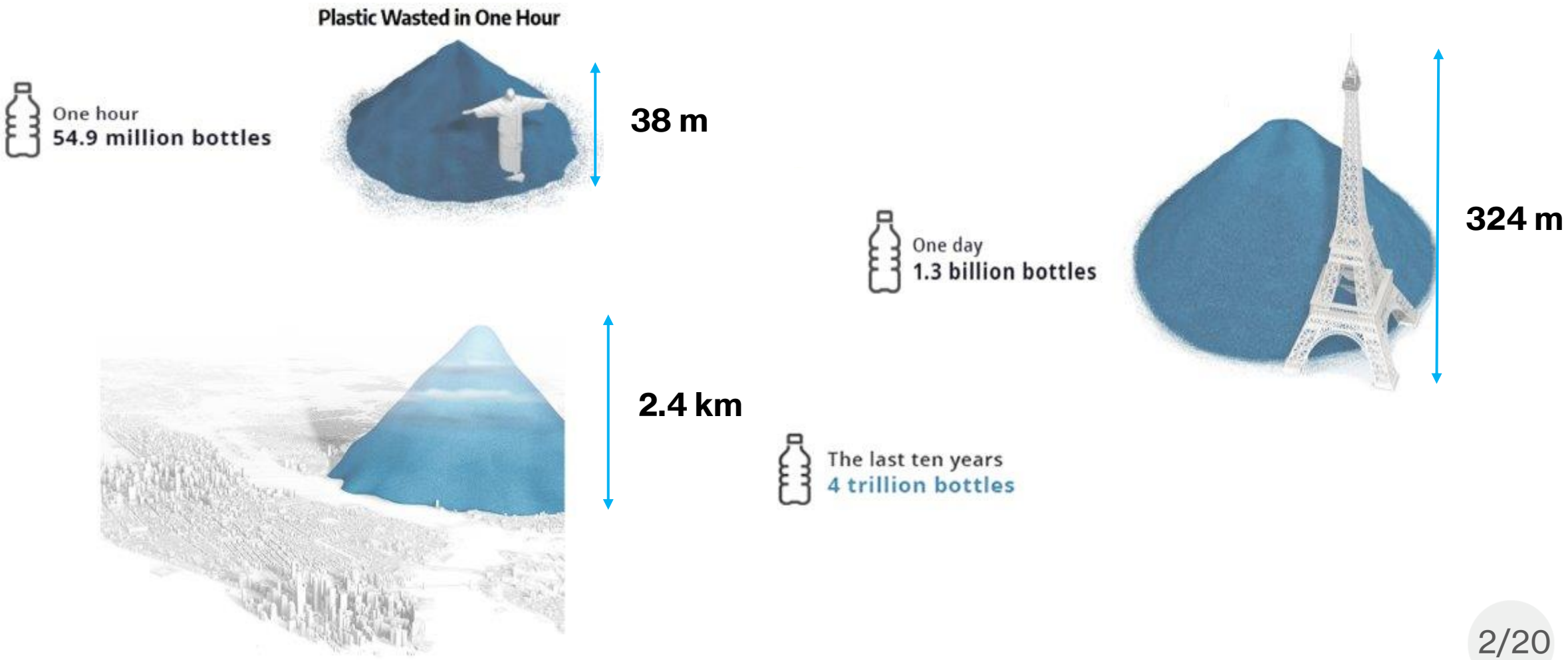


The elephant in the room

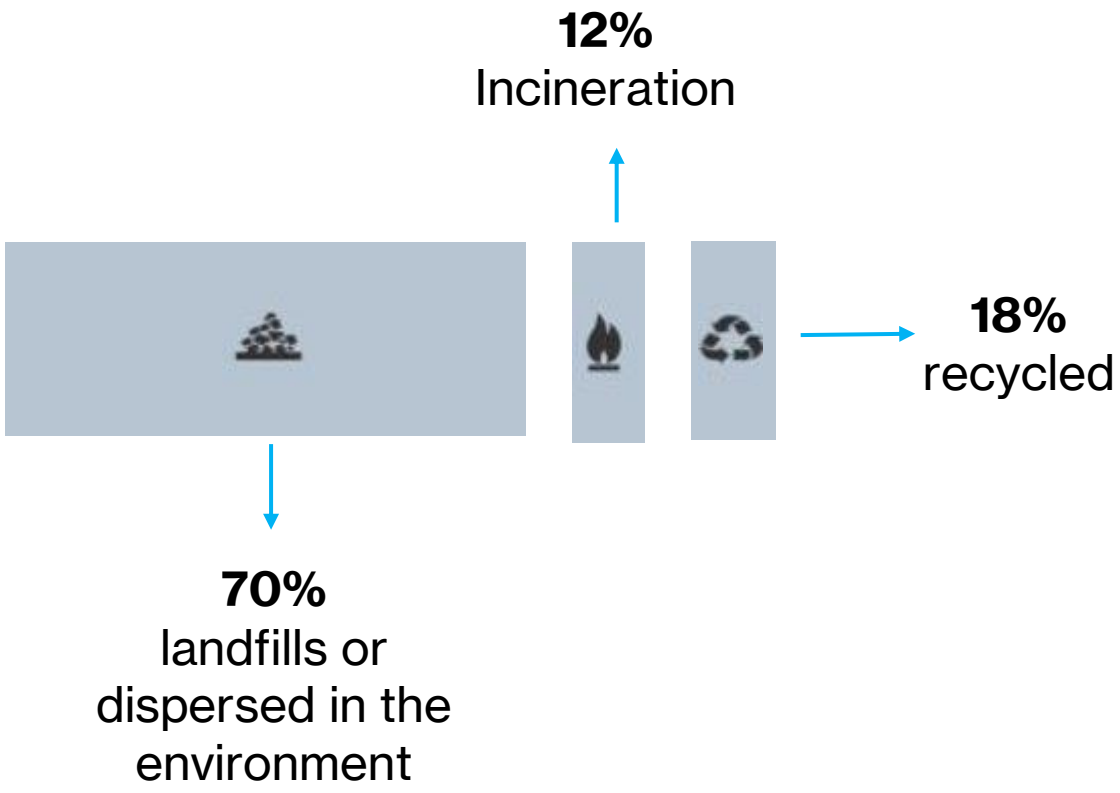
One hour
54.9 million bottles

The elephant in the room

The elephant in the room

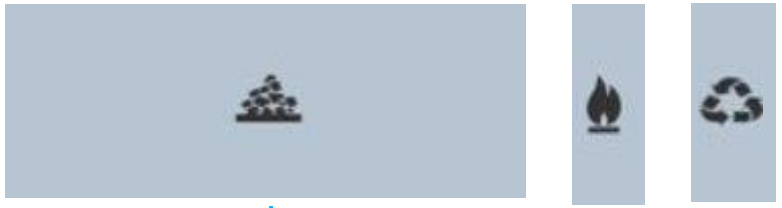


Where does all the plastic waste end up?



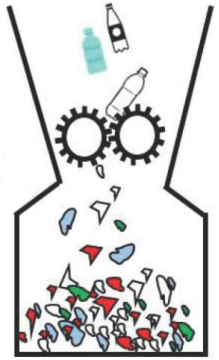
Where does all the plastic waste end up?

12%
Incineration



70%
landfills or dispersed in the environment

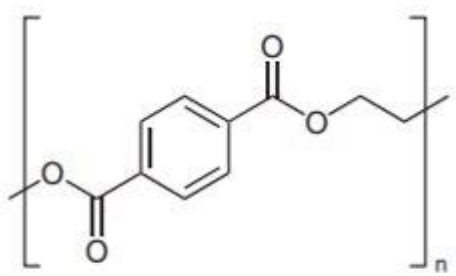
18%
recycled



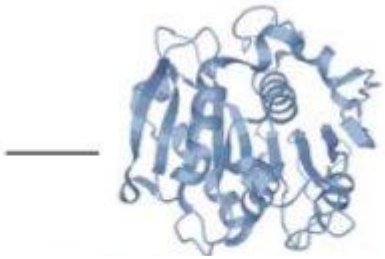
Mechanical recycling **downgrades** original material

Chemical recycling requires **toxic** catalysts

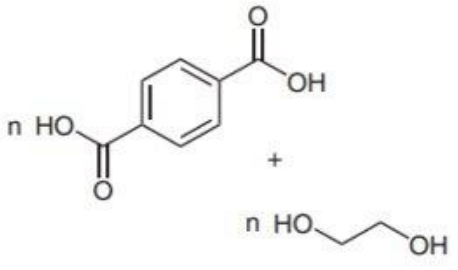
Is enzymatic degradation the solution?



Polyehtylene Terephtalate
(PET)

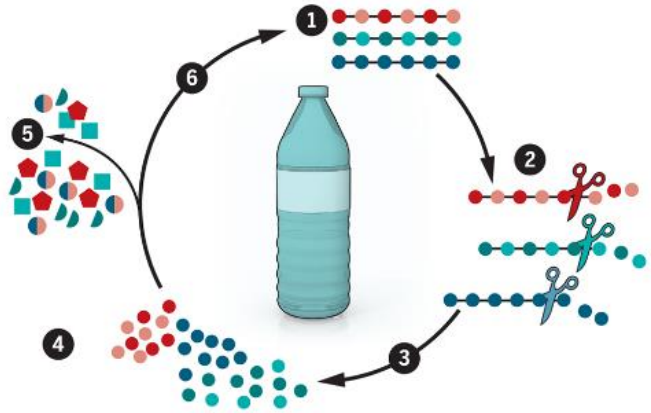


Enzyme

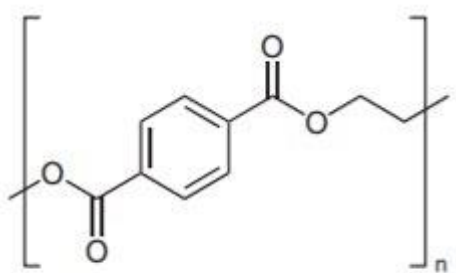


Monomers
(TPA + EG)

Circular Economy

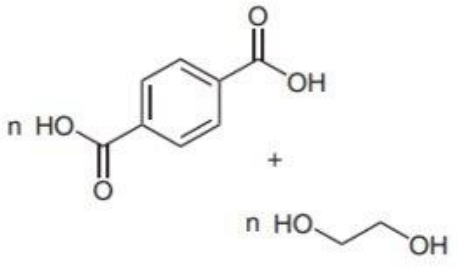


Is enzymatic degradation the solution?



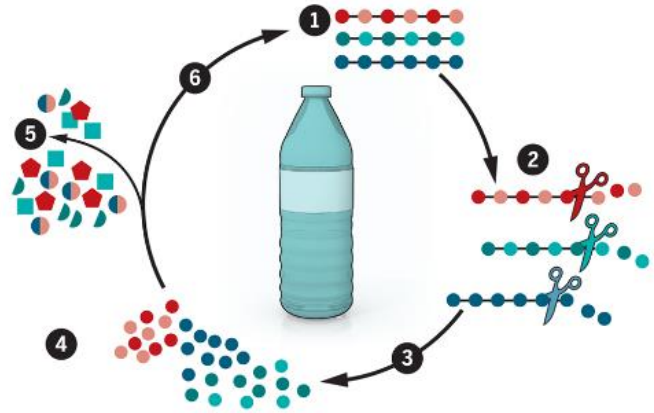
Polyehtylene Terephtalate
(PET)

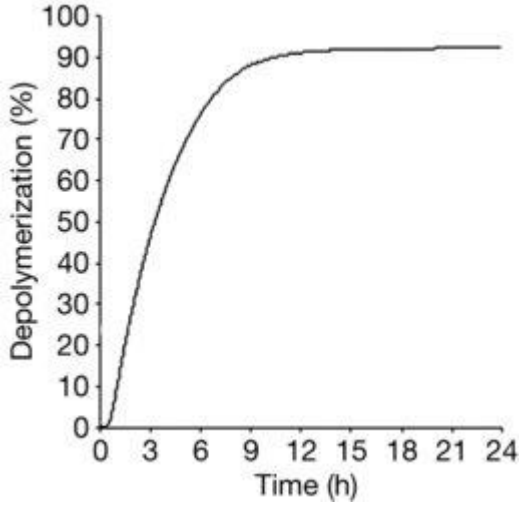
Enzyme



Monomers
(TPA + EG)

Circular Economy

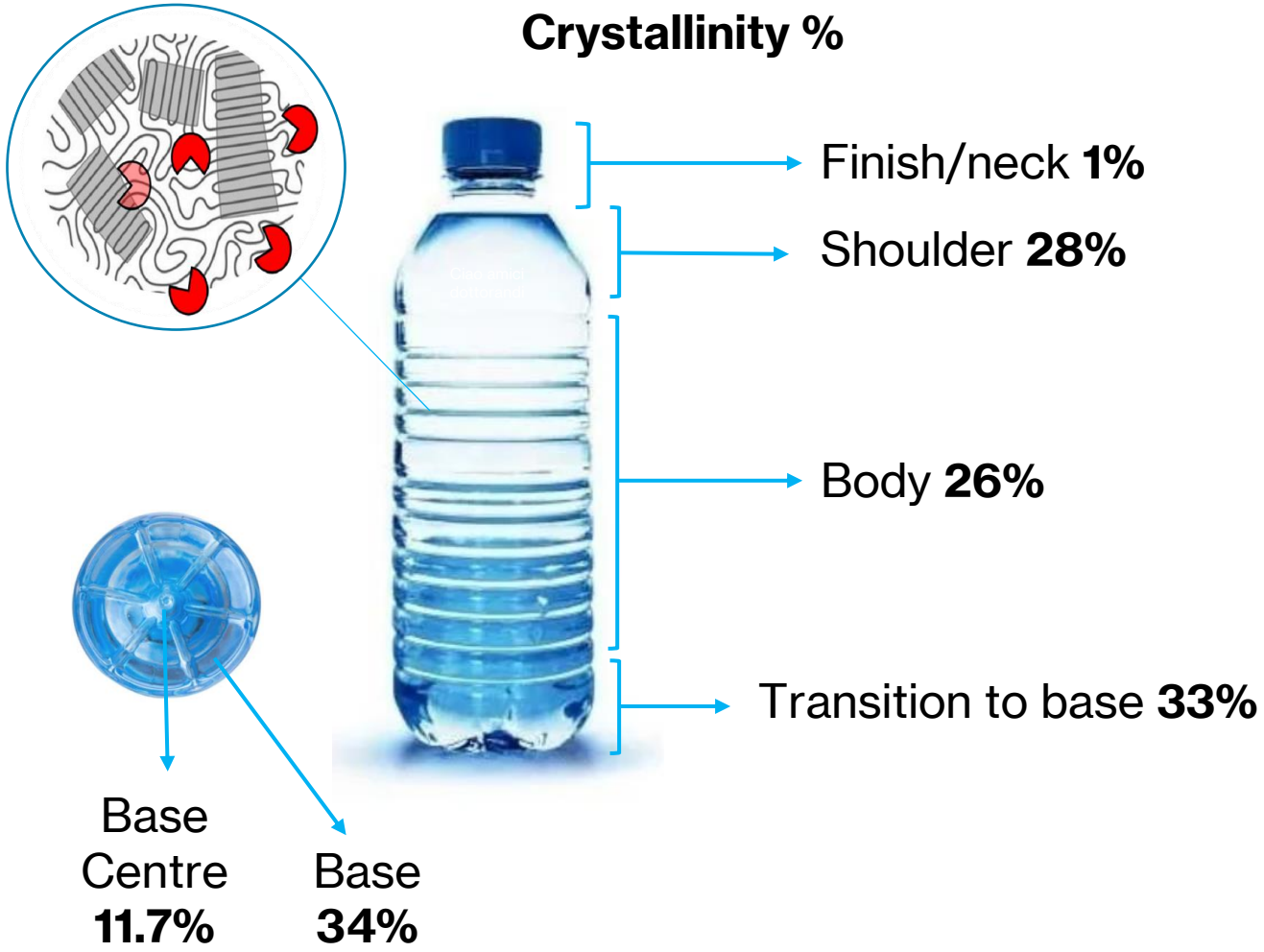




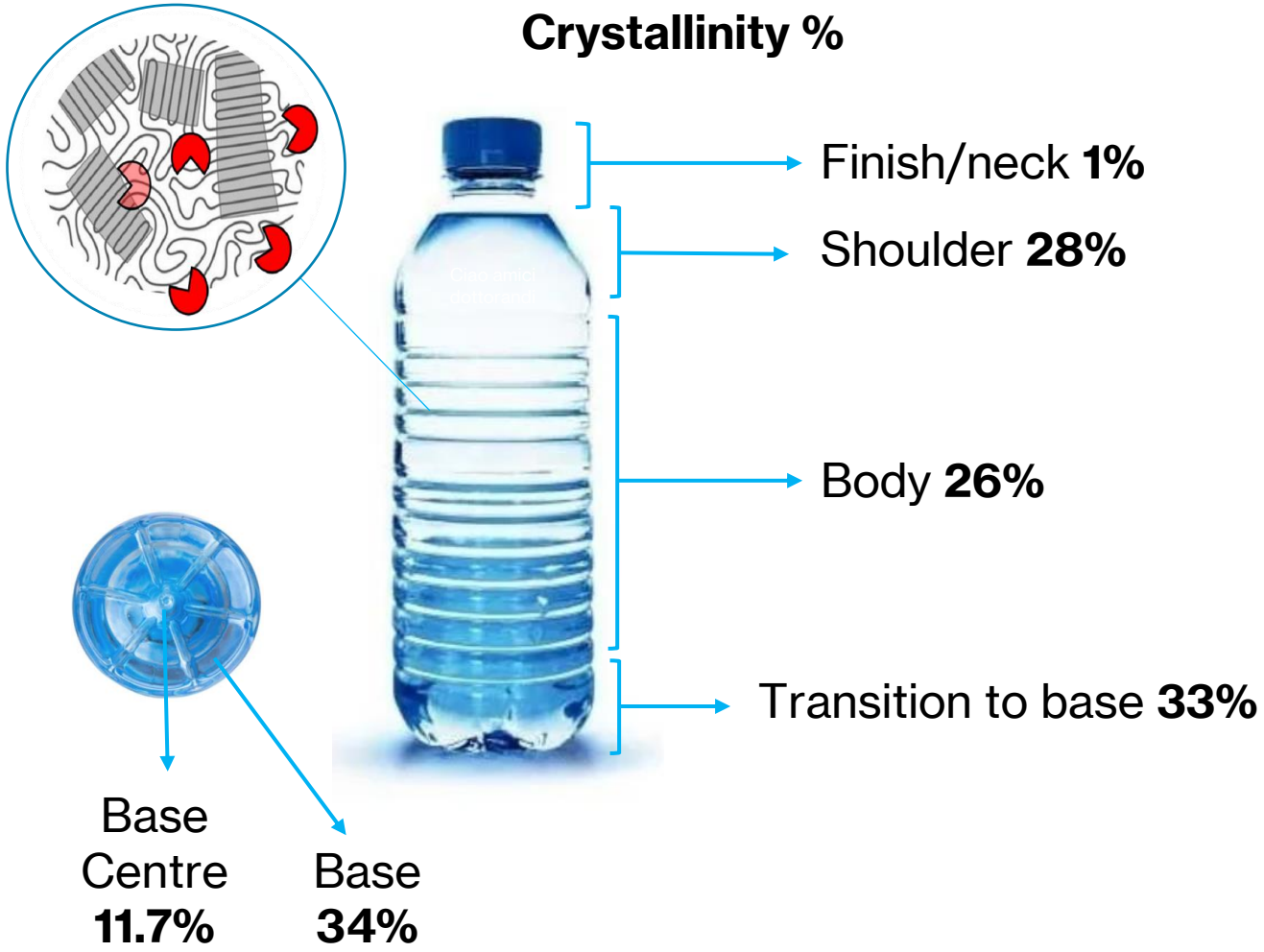
LCC^{ICCG} depolymerize **90% of amorphous PET powder** at 72°C[1]

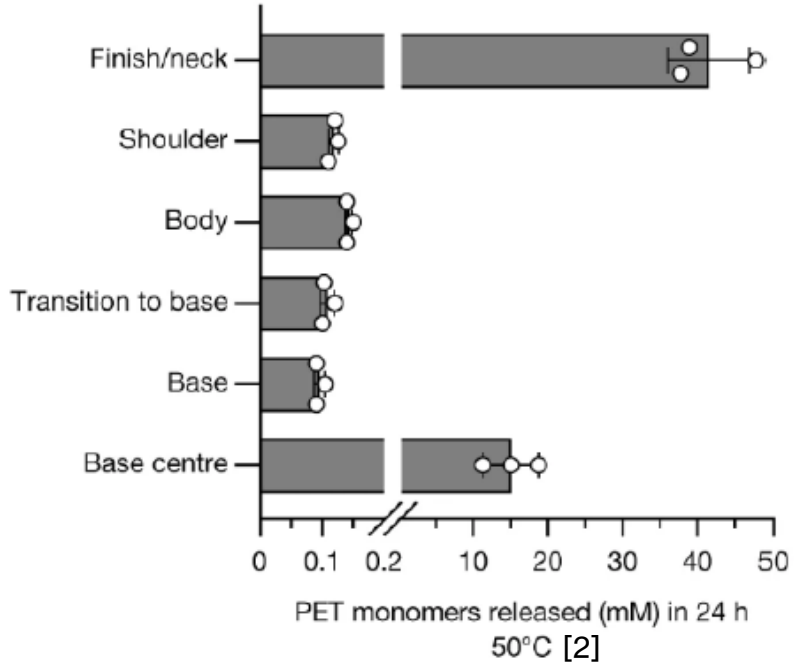
*[1] Tournier et al. Nature, **580**, 216–219 (2020)*

Crystallinity is critical for degradation



Crystallinity is critical for degradation





Degradation is **anticorrelated** with crystallinity!

[2] Lu et al. Nature, 604, 662-667 (2022)

Crystallinity is critical for degradation

PET physical properties	
Melting point	~ 260 °C
Tg	~ 75-80 °C
Tg (in H_2O)	~ 65 °C

→ Amorphization is energy-**expensive**!

Crystallinity is critical for degradation

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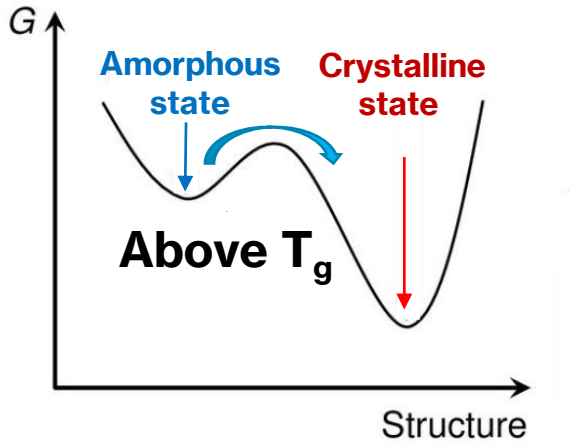
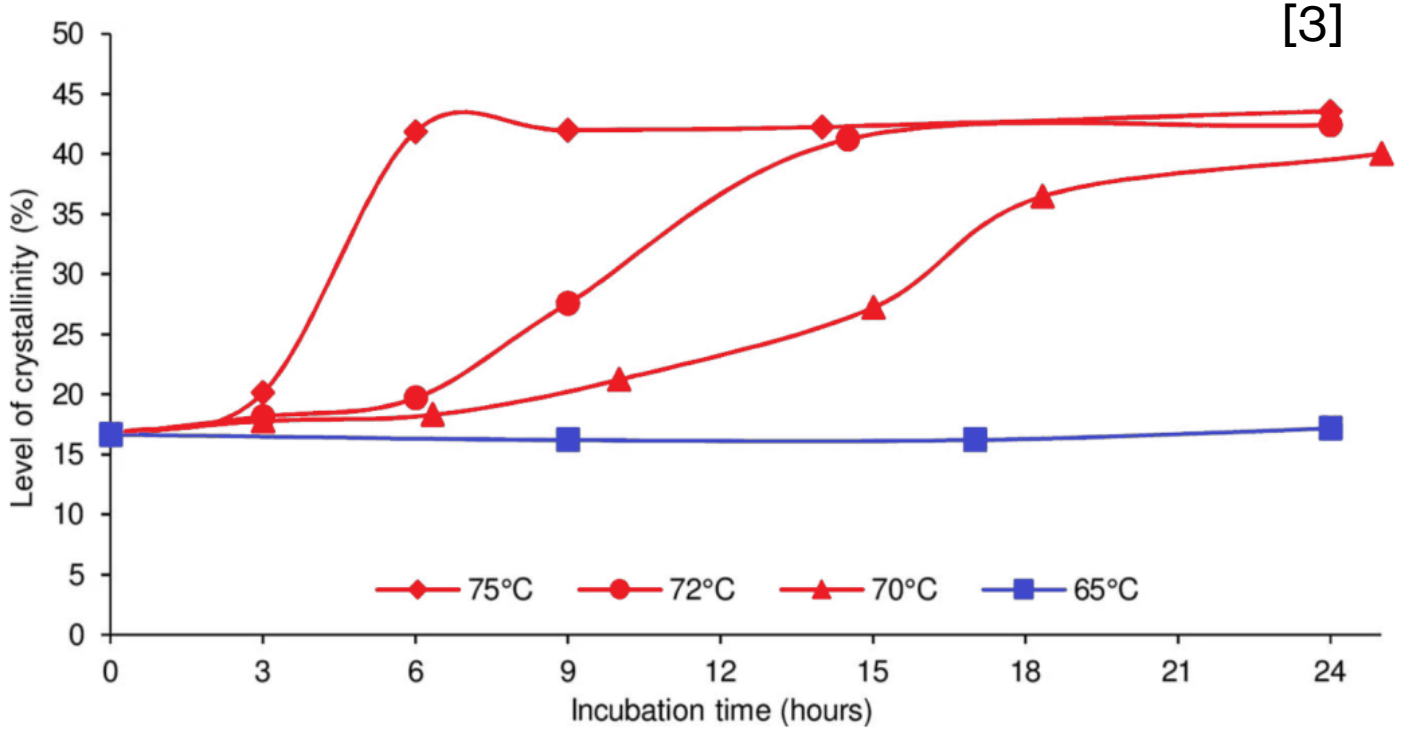
Melting point	~ 260 °C
Tg	~ 75-80 °C
Tg (in H_2O)	~ 65 °C



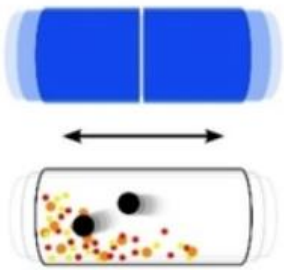
[3]



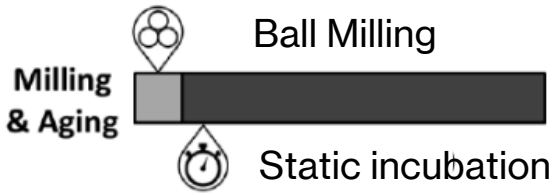
*[3] Tournier et al. Nature, **580**, 216–219 (2020)*

Project Goals

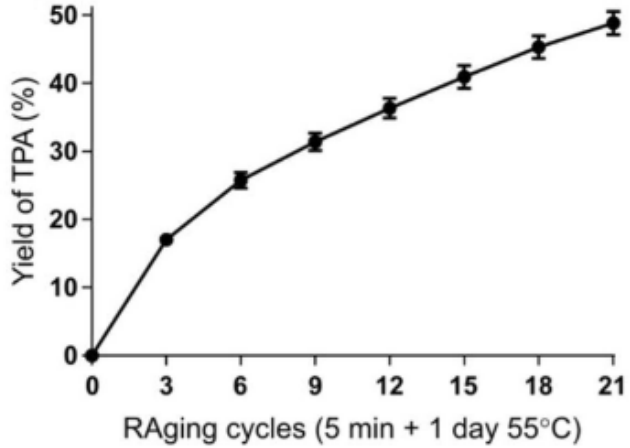
01 Expand understanding of degradation in **moist-solid** reaction mixture



η = 1.5 µL/mg



[4] Kaabel et al. PNAS 118 (29), (2021)



02 Develop a green efficient **pre-treatment** to improve enzymatic attack

Materials

Cutinase from **Humicola Insolens** (HiC)
(STREM chemicals)

poliplast S.p.A.

0-150 µm

150-300 µm

CL767

300-500 µm

500-1200 µm

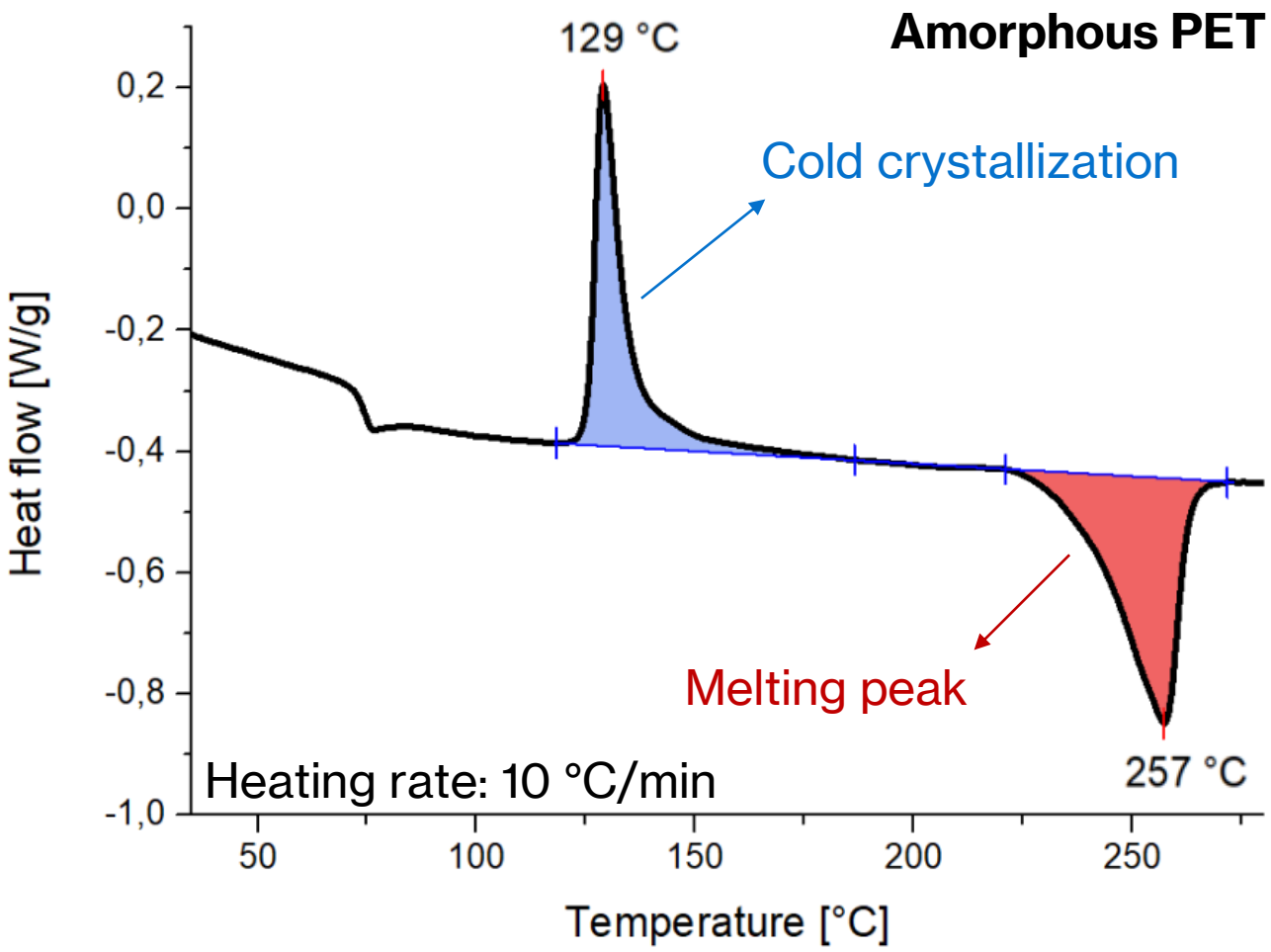
PET powder

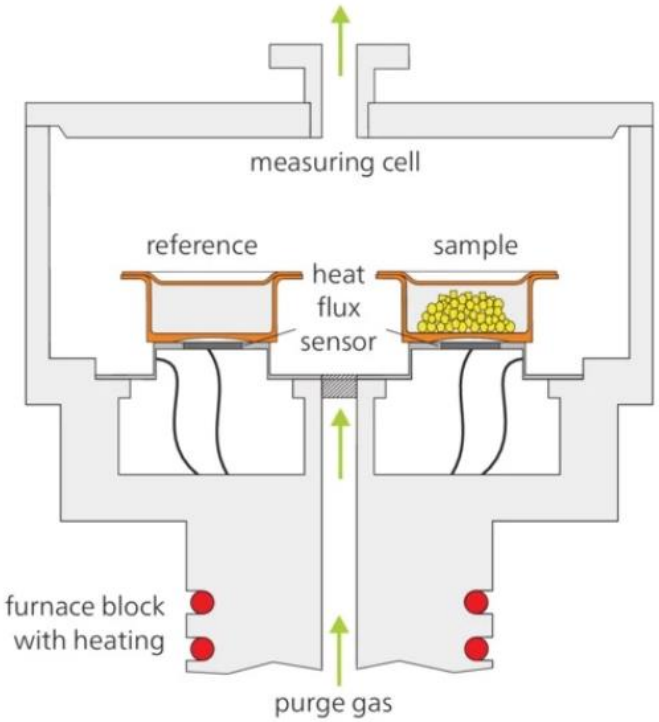
Am PET

MPET

PET granules

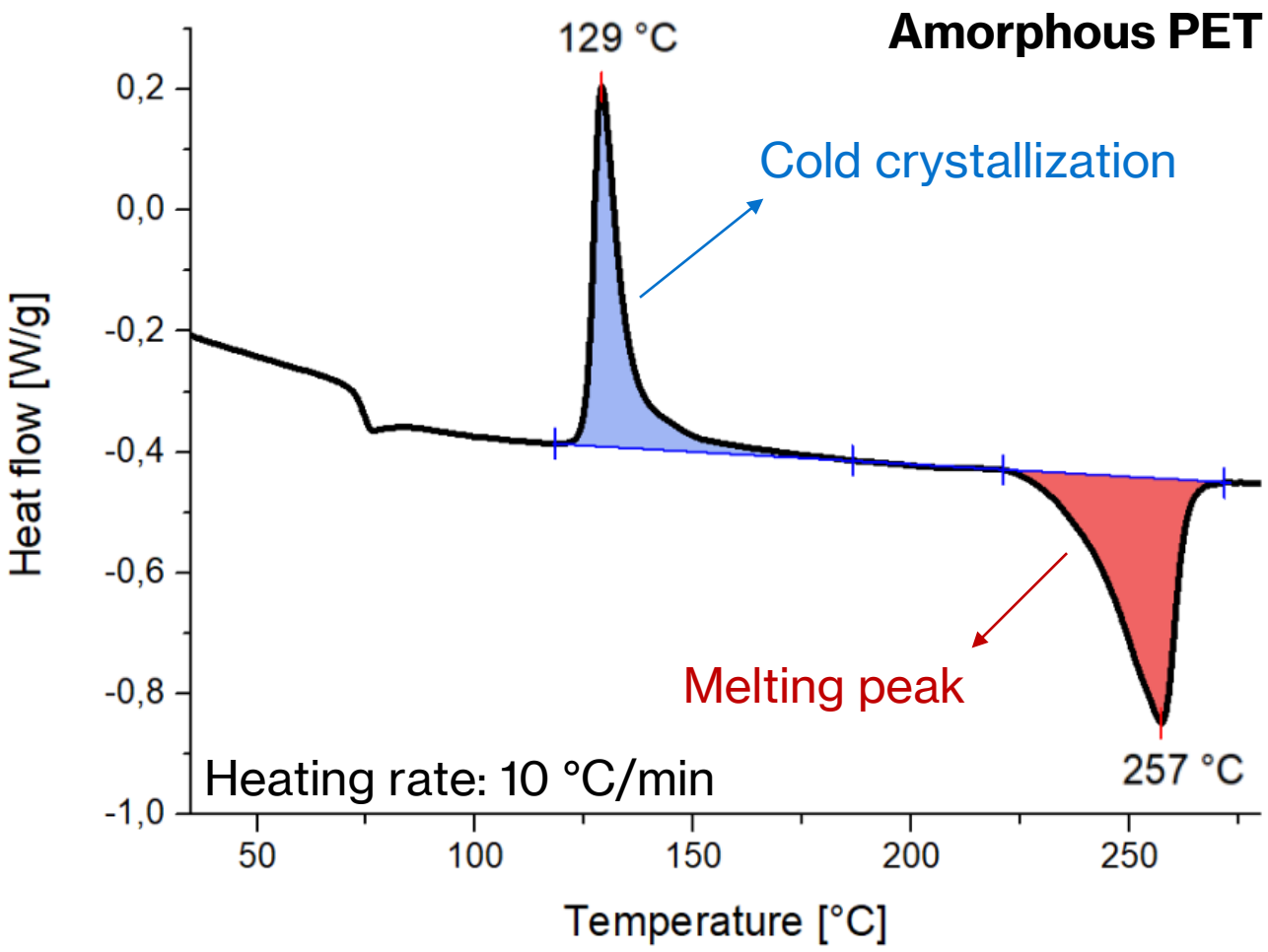
DSC characterization





Differential scanning calorimetry (DSC) apparatus

DSC characterization



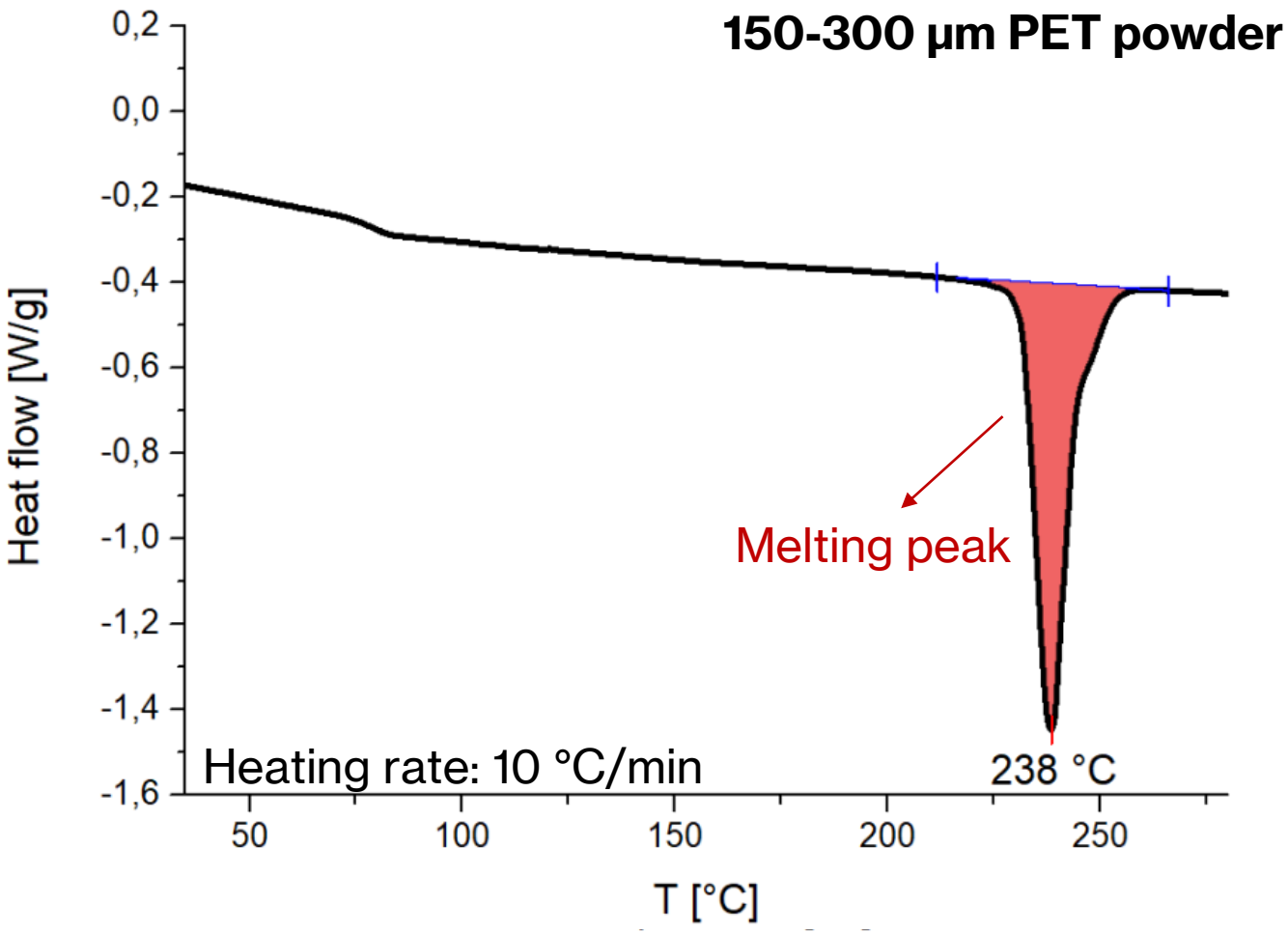
Crystalline fraction (X_c):

$$X_c = \frac{\Delta H_f - \Delta H_{cc}}{\Delta H_f^0}$$

With ΔH_f^0=140.1 J/K

Sample	Crystallinity %
Am PET (granules)	8.7±0.5

DSC characterization



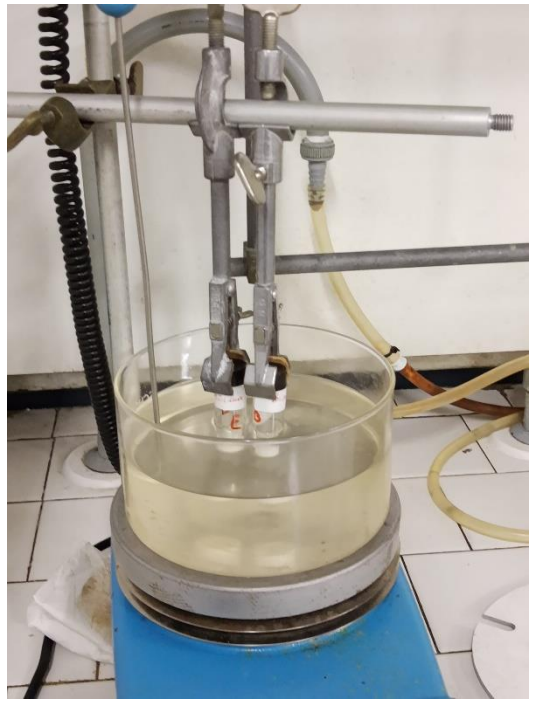
Crystalline fraction (X_c):

$$X_c = \frac{\Delta H_f}{\Delta H_f^0}$$

With ΔH_f^0=140.1 J/K

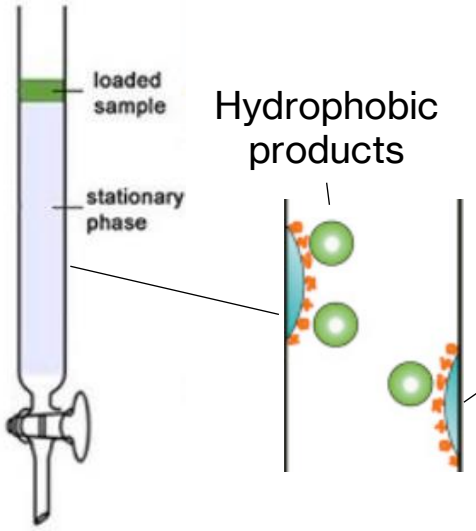
Sample	Crystallinity %
0-150 µm	40 ± 2
150-300 µm	41 ±1
300-500 µm	42 ± 1
500-1200 µm	40 ± 2
MPET (granules)	41 ± 2

Testing enzyme activity



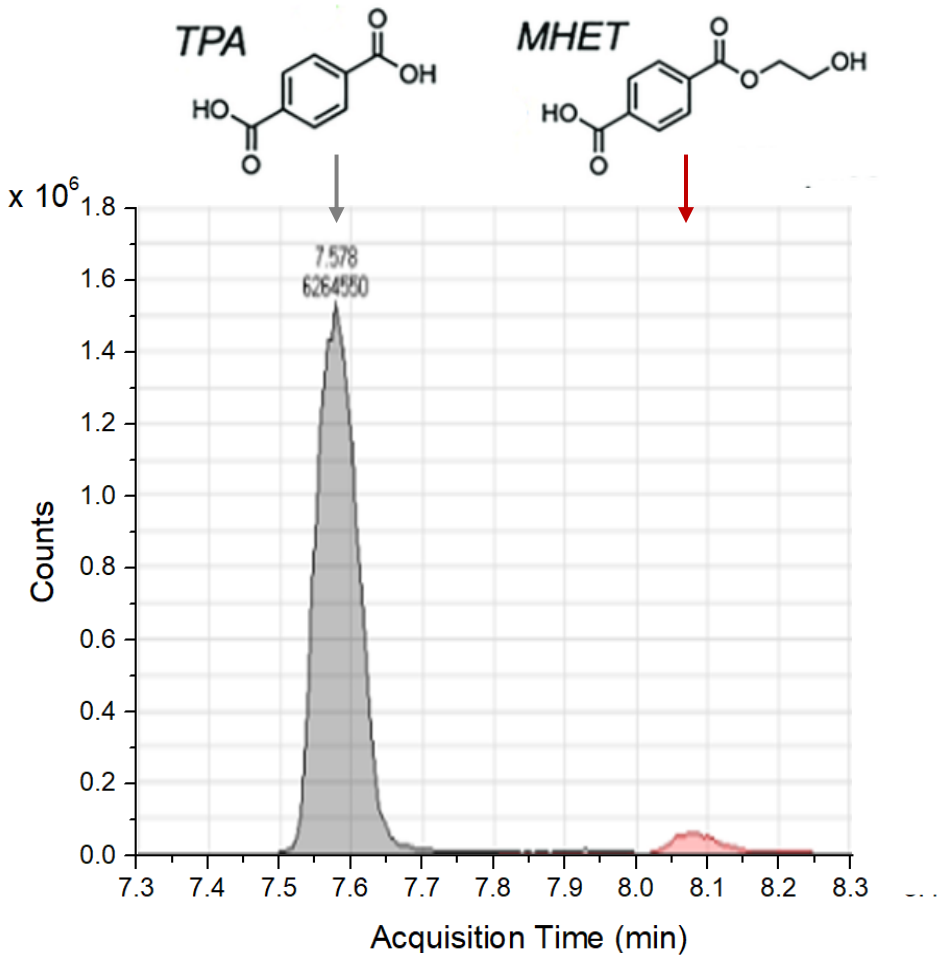
Oil bath at **55°C,** agitation provided through **magnetic stirring**

Product quantification through **HPLC**



Hydrophobic products

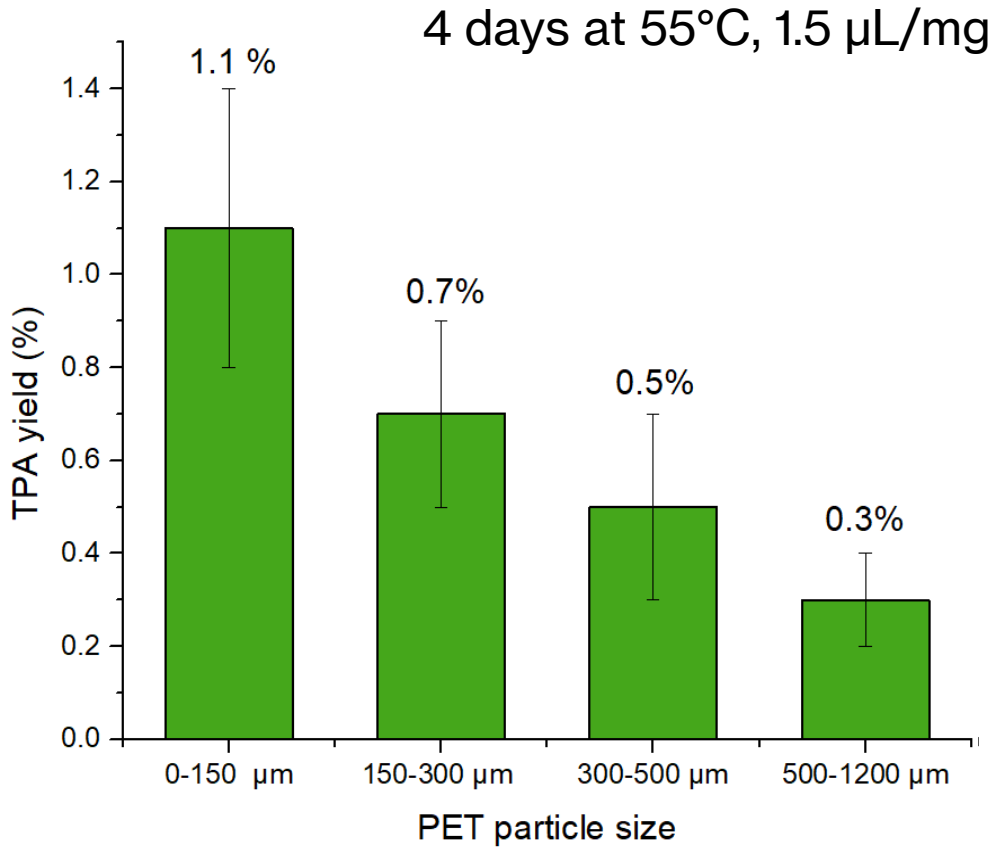
Silica beads with C_{18} alkyl chains



MH MOLECULAR HORIZON

01 Testing enzyme activity

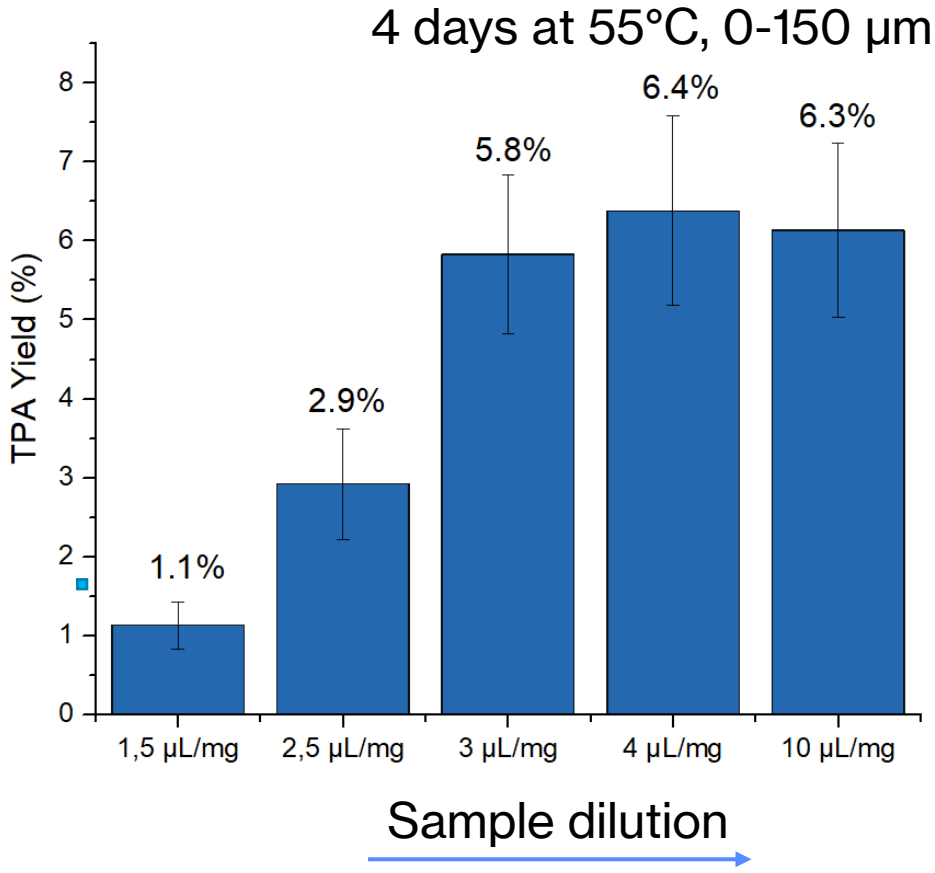
1. TPA yield is sensitive to **particle size**



01

Testing enzyme activity

1. TPA yield is sensitive to **particle size**
2. TPA yield **increase** with dilution

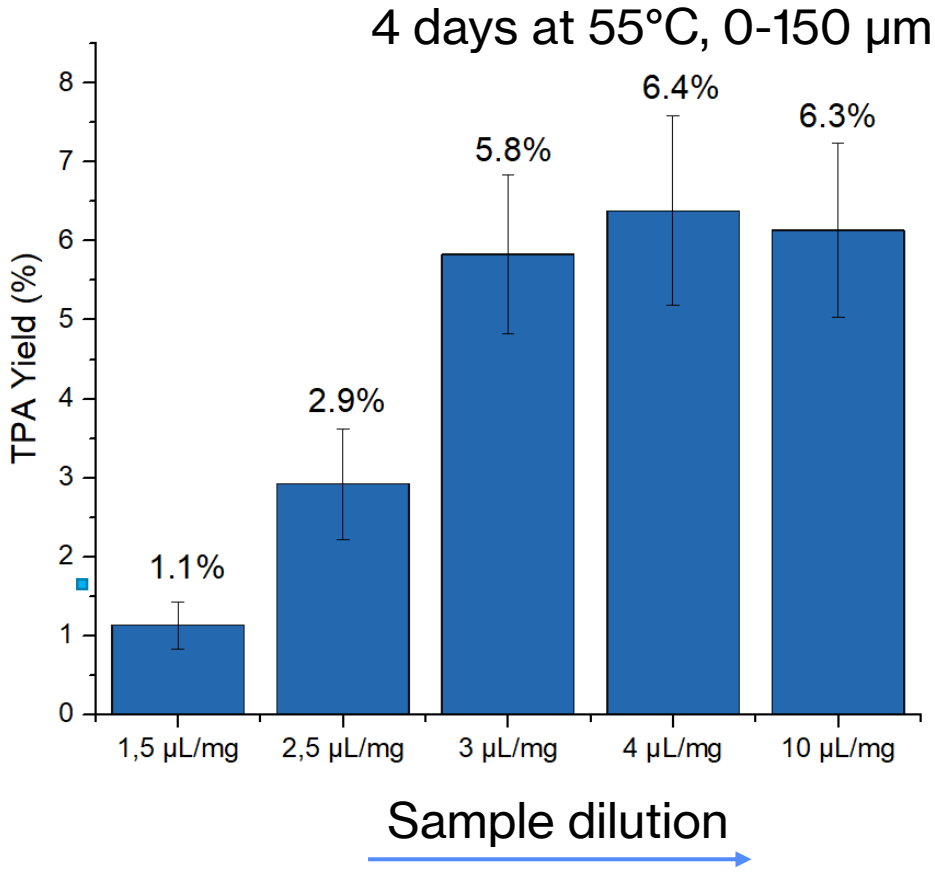


01

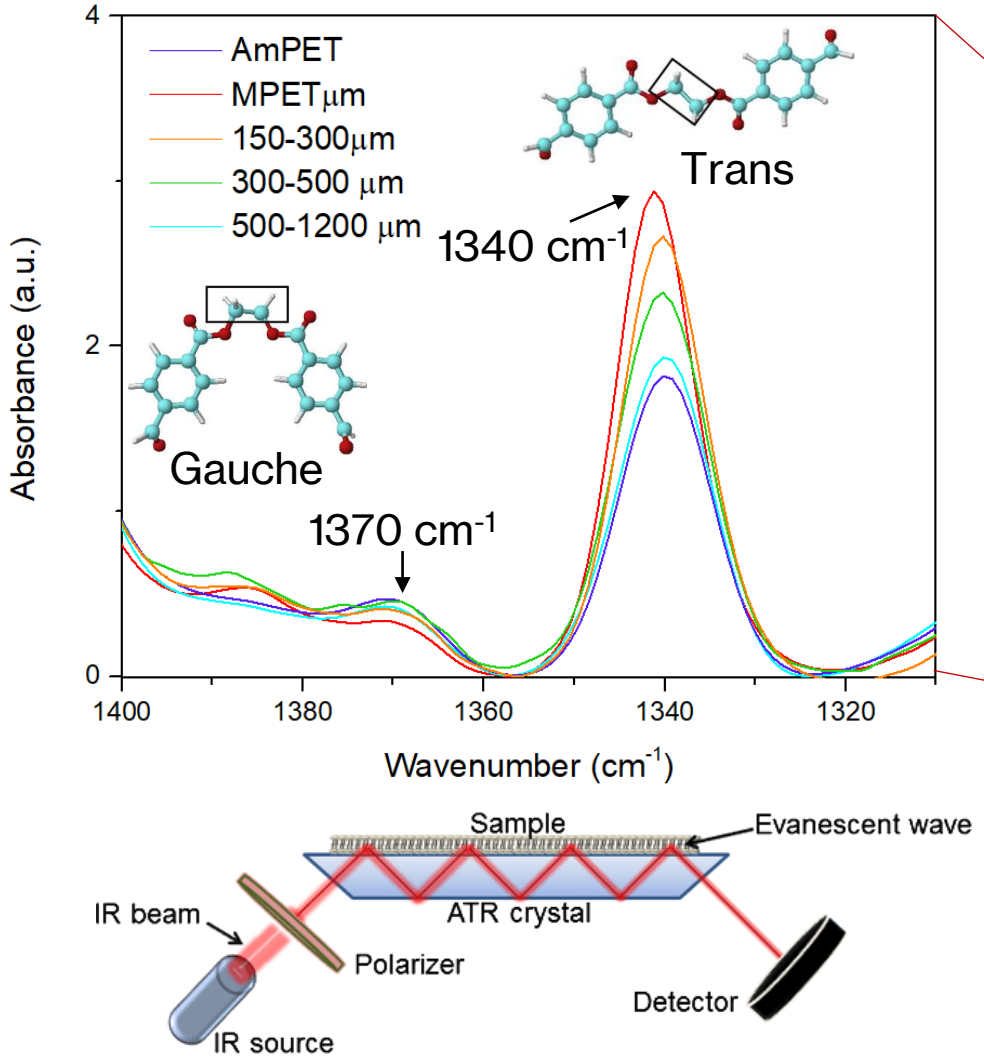
Testing enzyme activity

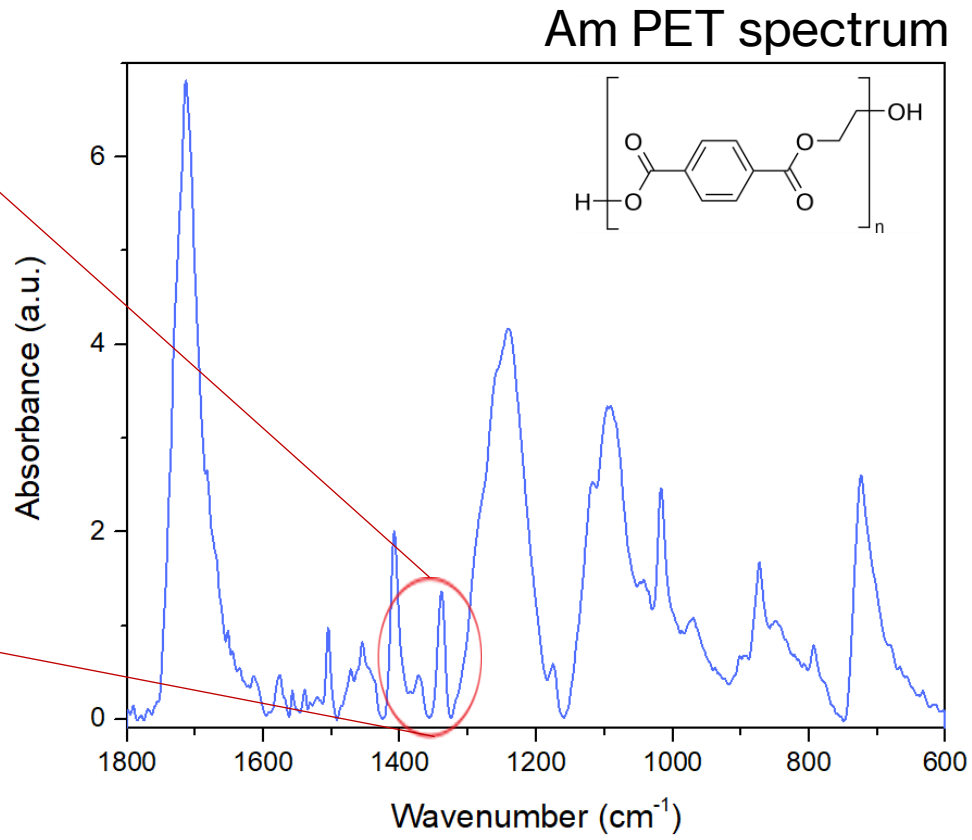
1. TPA yield is sensitive to **particle size**
2. TPA yield **increase** with dilution
3. Literature results are not reproduced by **magnetic stirring**

The role of **ball milling** must be further investigated

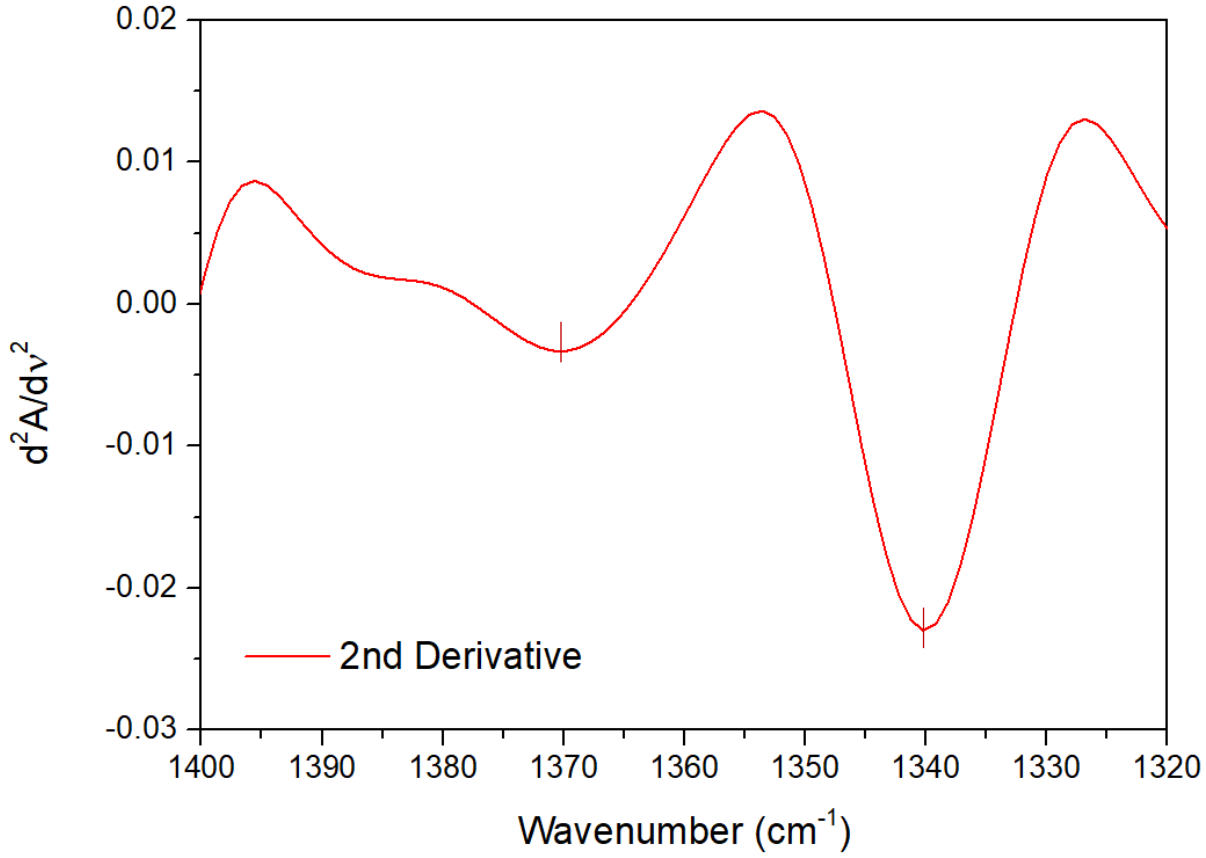


Crystallinity analysis with ATR-IR spectroscopy





Second derivative analysis



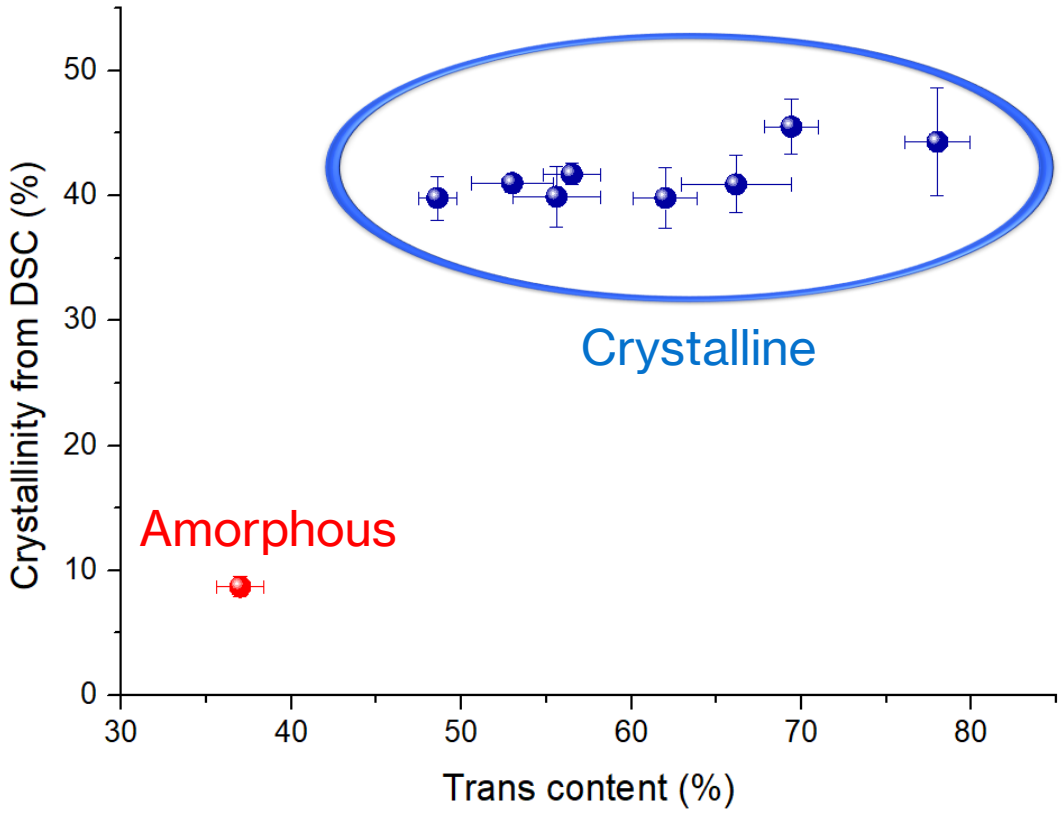
Trans conformer fraction T(t) can be determined as:

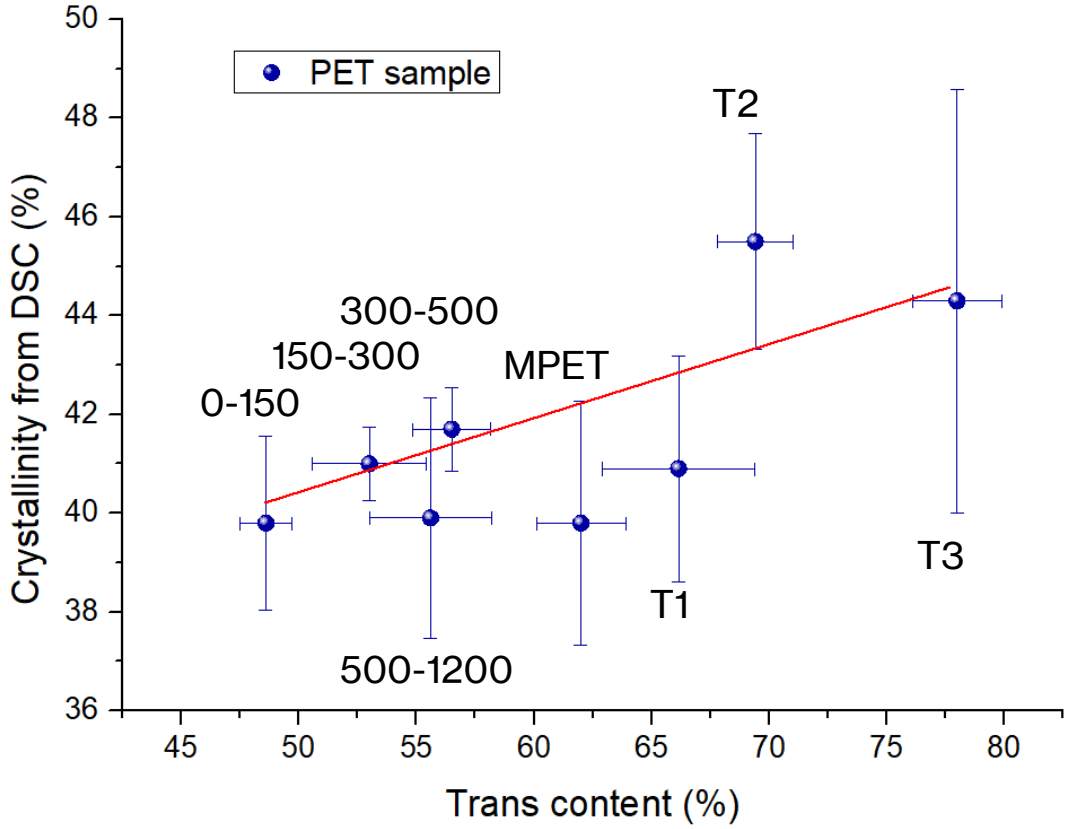
$$T(\%) = \frac{c_{trans}}{c_{trans} + c_{gauche}} = \frac{A_{1340}}{A_{1340} + kA_{1370}}$$

Where:

$$k = \frac{\epsilon_{1370}}{\epsilon_{1340}} = 6.7$$

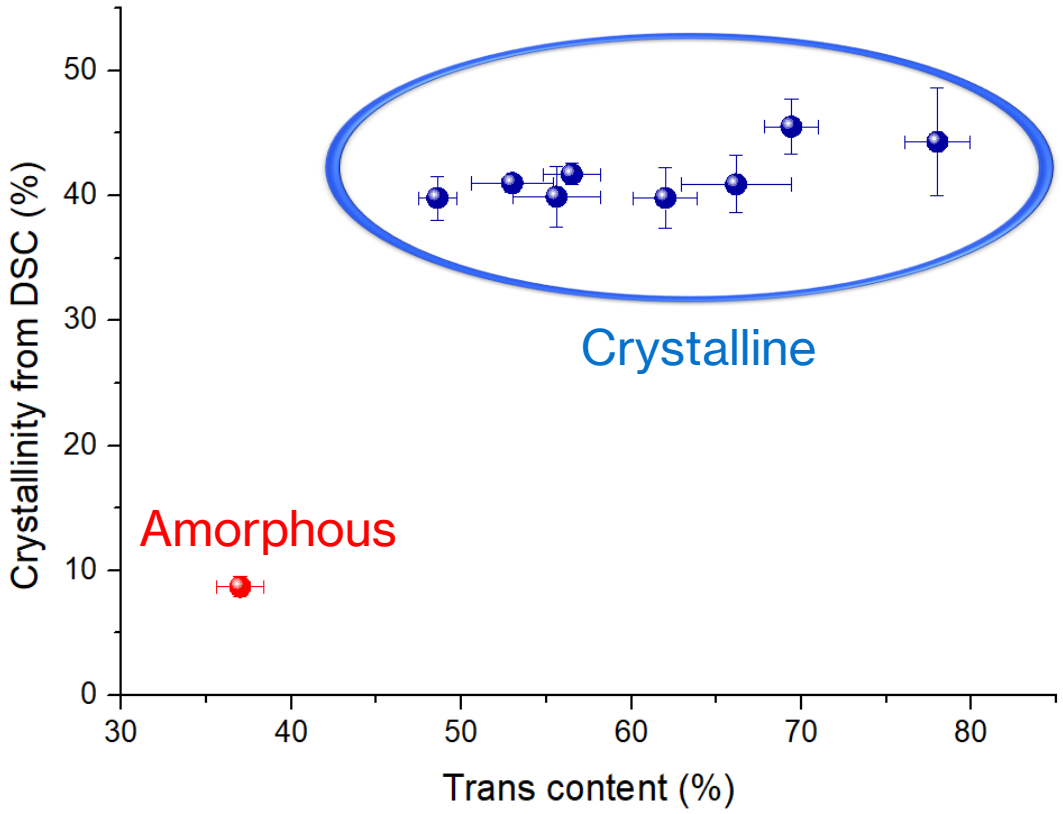
DSC vs ATR-IR

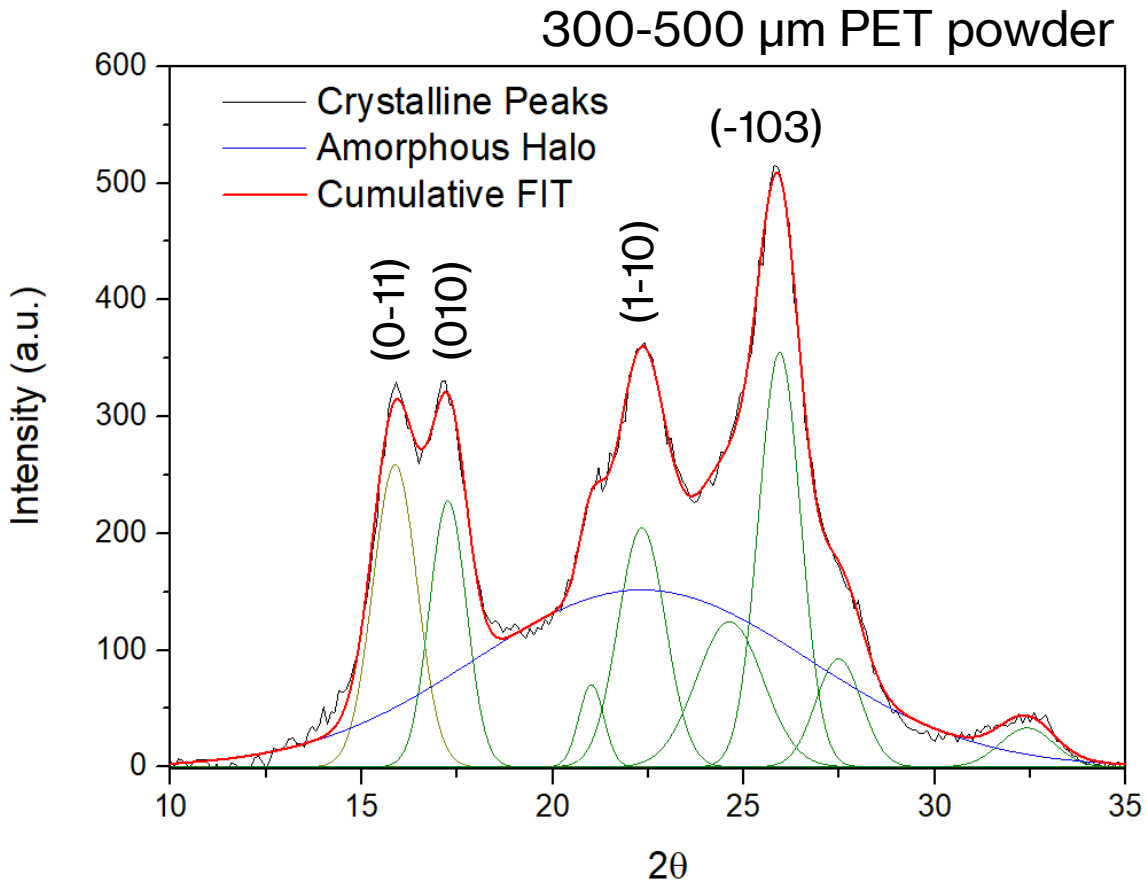




Linear FIT	
Intercept	33 ± 3
Slope	0.15 ± 0.05
R	**0.68**

DSC vs ATR-IR





XRD data are currently being acquired!

02

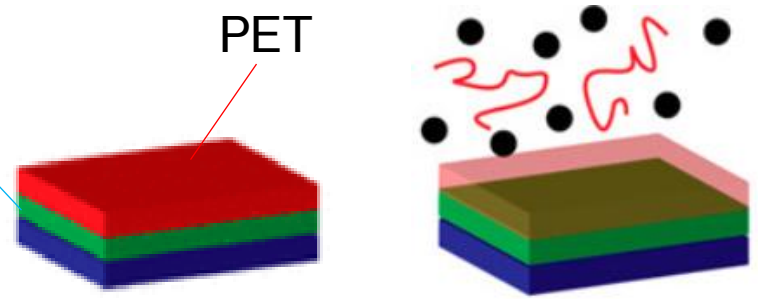
PET pre-treatment

Selective dissolution
and
Precipitation

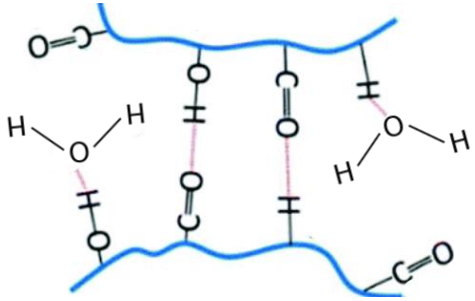
Solvent patented by
Redantea srl

- Inexpensive
- Biodegradable
- Non volatile

Polyaddition
polymers
(PE, PP, PS)

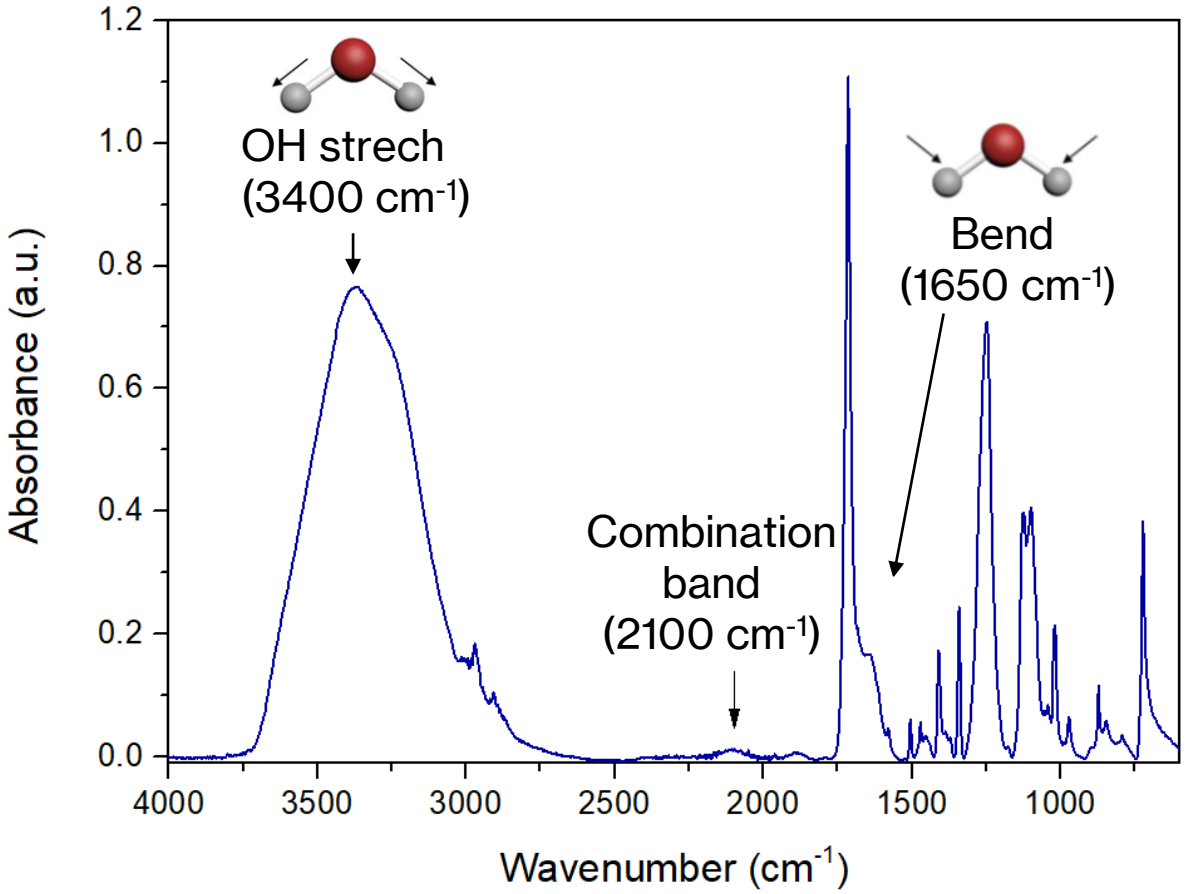


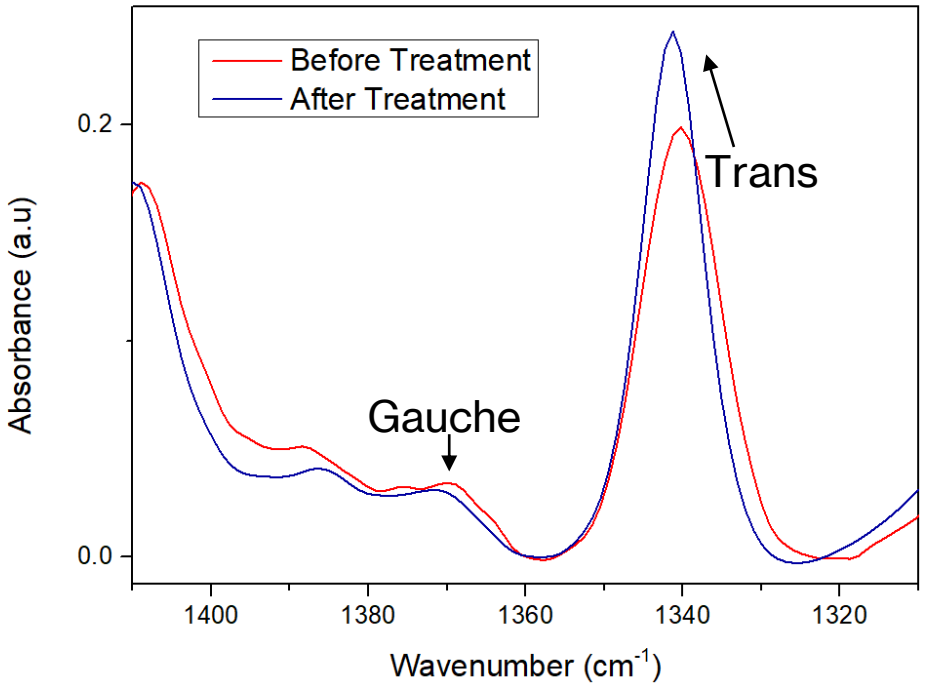
Recycling of mixed plastic waste



Improve accessibility

PET pre-treatment



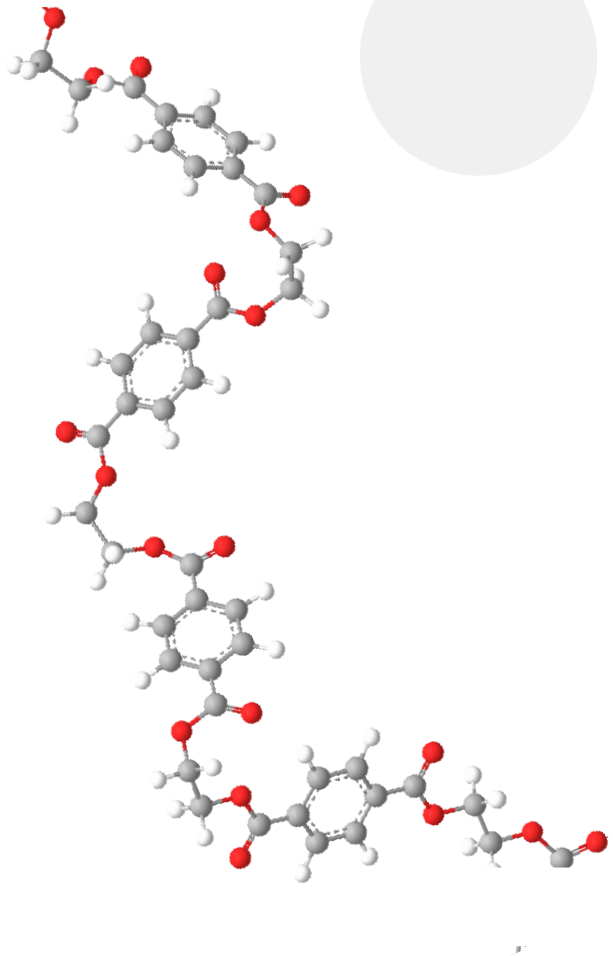


- Signals from **absorbed water**
- ~20 fold **weight increase**

  5g ⟶ 98 g
- **Trans** content increase

Next Steps

- Test how **ball milling** affects enzymatic reactivity
- **XRD** characterization of samples
- Study how **IR spectrum** change upon degradation
- Evaluate the effectiveness of the **pre-treatment**



1st year educational activities

Courses attended

1. **Uncertainty and probability** (G. d'Agostini)

2. **Effective field theory:**
   -Theoretical introduction to EFT (D. Buttazzo)
   -Effective gauge theory in spintronics (G. Tatara) ✓

3. **Nanosystems and advanced Materials:**
   -Molecular nanomagnets (E. Garlatti, A. Chiesa) ✓
   -Raman spectroscopy (F. Ripanti)
   -Spectroscopy characterization of nanostructured materials (M. Pedio)

4. **Teaching and learning Physics** ✓
   (G.Organtini)

5. **Multimessanger astrophysics:** ✓
   - *Gamma rays* (G. Tosti)
   -Gravitational waves (M. Punturo)
   -Neutrinos (S. Germani)

6. **Introduction to space physics**
   (N. Tomassetti)

1st year educational activities

Other activities

Schools:

- Winter school in Biotechnology 8° edition, Perugia, 17-21 January 2022

Conferences:

- Mechanochemistry: Fundamentals, applications and future, Faraday Discussion, 12-14 September 2022, Cambridge (UK)
- XLII National Congress of SISFA (organizing committee)

Relevant seminars:

- Plastics in the environment (R. Kuhlman)

Didactics:

-Tutor for the physics course at the department of agricultural, environmental and food sciences
- "Cultore della materia" for the physics course within the biotechnology bachelor's degree

Thank you for your attention