

A Platform to Upcycle and Recycle Various Grades of PE by C-H Activation

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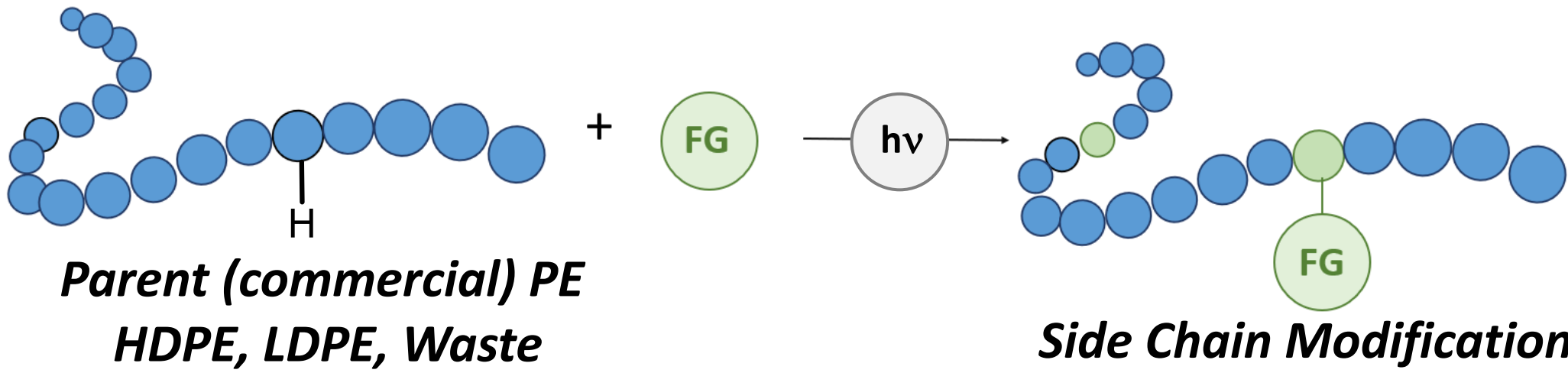
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INTRODUCTION

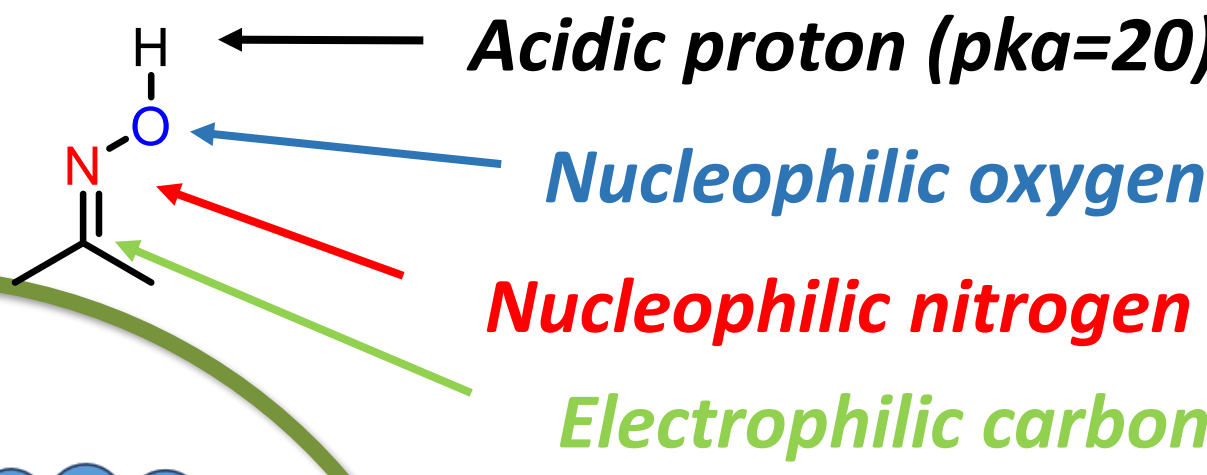
- Polyethylene (PE) : **150 million tons** produced every year.¹
- Chemical recycling: hindered by the simplicity of its structure (inert C–C and C–H bonds).²
- This work : aims at incorporating polar functional groups into PE chains via selective, **Metal-free C-H activation** under mild conditions. ³
- This strategy : enabling high-value material production with improved properties and easier PE deconstruction : via incorporation of cleavable C–X bonds in the backbone.

Post-Polymerization Modification by C-H Activation-Upcycling



OUR STRATEGY

- The incorporation of **ketoxyimes** into PE through C-H activation offers a **platform** to modify PE properties.



- Not susceptible to hydrolysis
- Versatile scaffold

Methodology :

Alkane models
(C7,C24,C40)

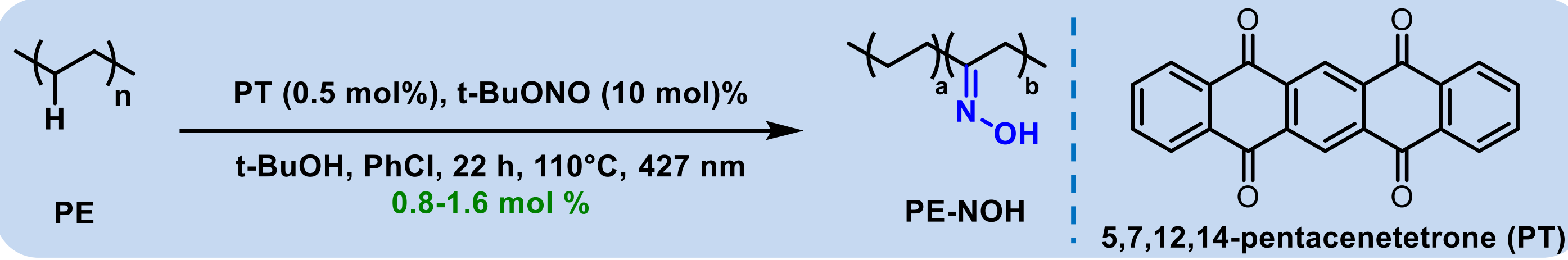
Tailored low Mn
polymethylene

Commercial PE (HDPE,
LDPE, LLDPE)

Post-consumer PE
(Waste)

PHOTO-NITROSATION^{4,5}

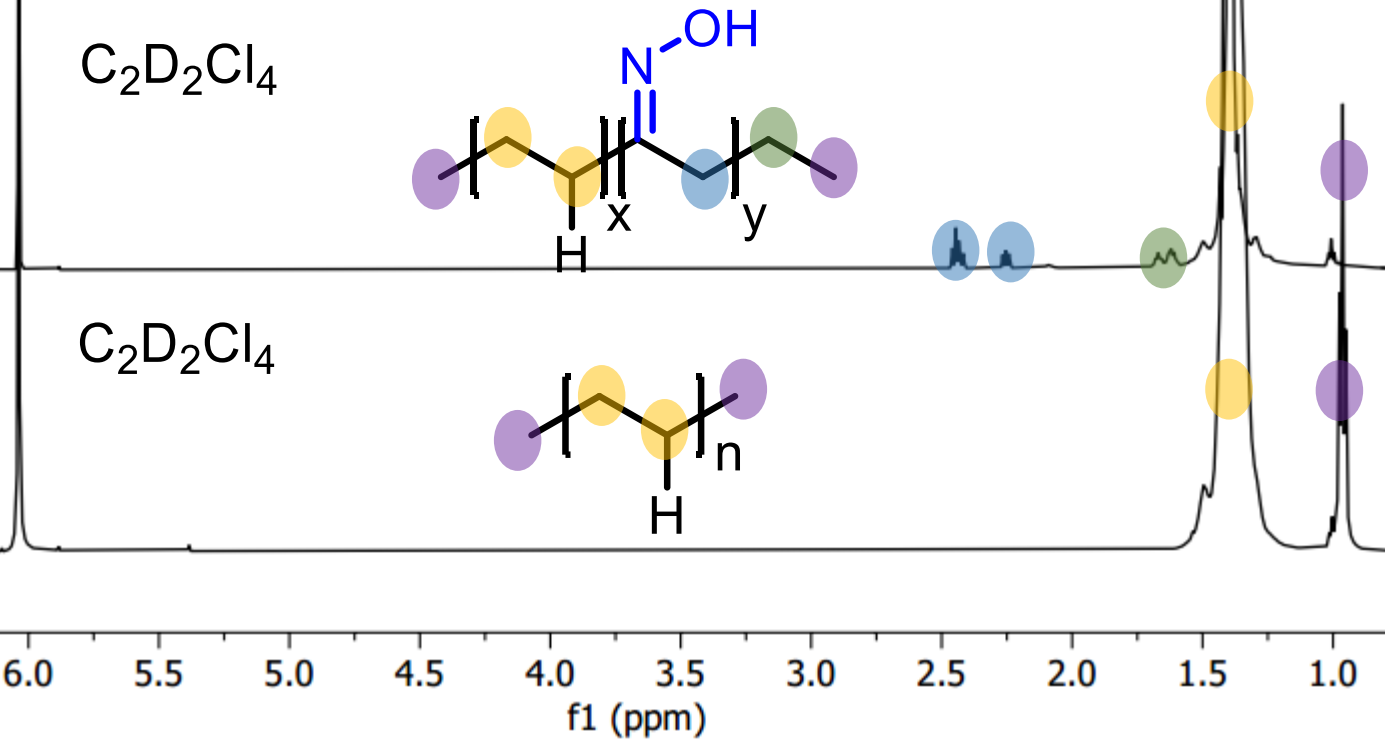
- Conditions :



- **Commercially available reagent**
- **Nitroso group transfer agent**

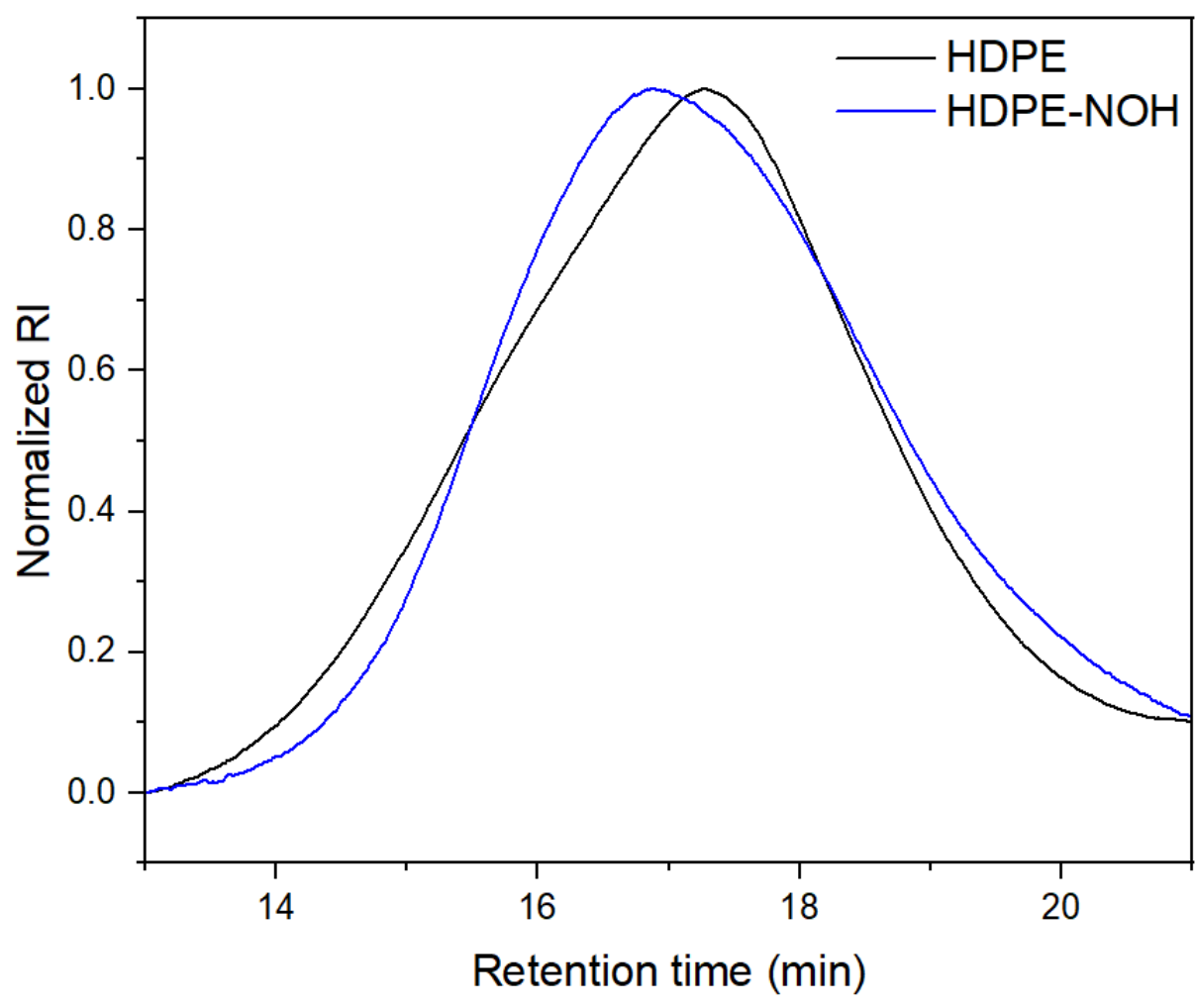
- Characterizations :

¹H NMR



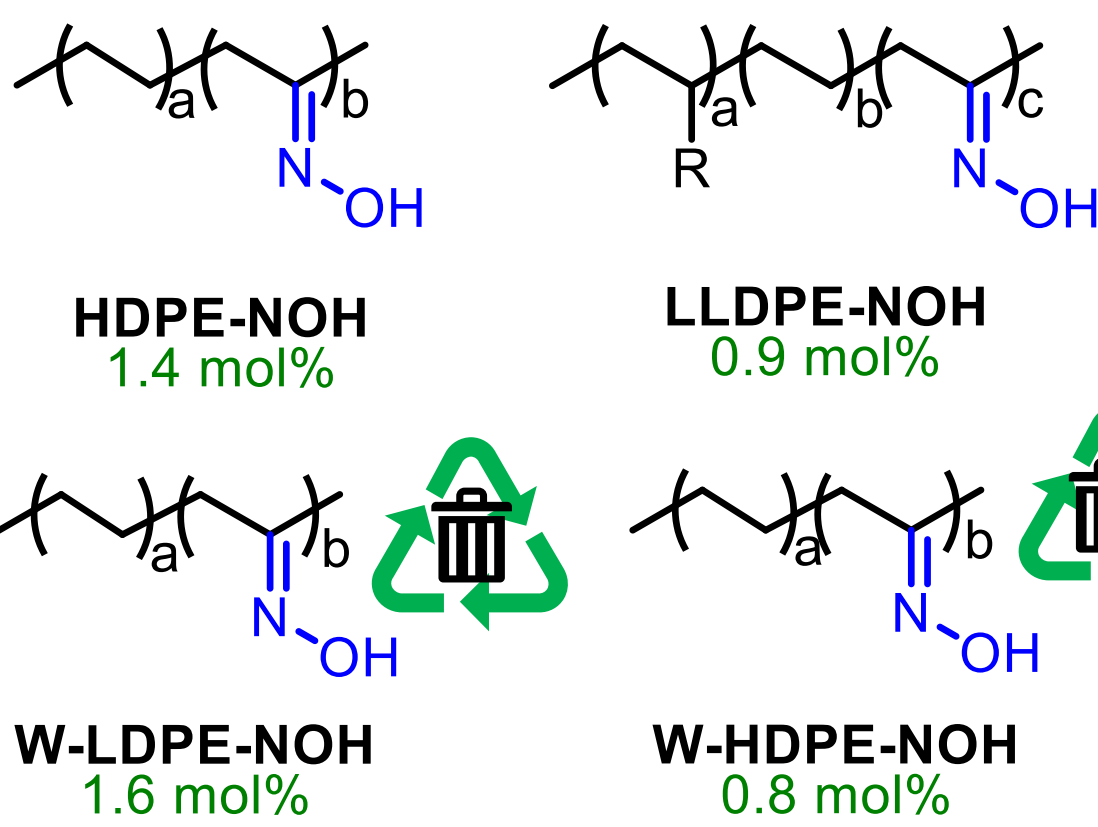
- Ketoxime's characteristic peaks visible after reaction

GPC



- Mn and PDI of modified HDPE were nearly identical to those of unmodified HDPE

Applicable to various PE grades

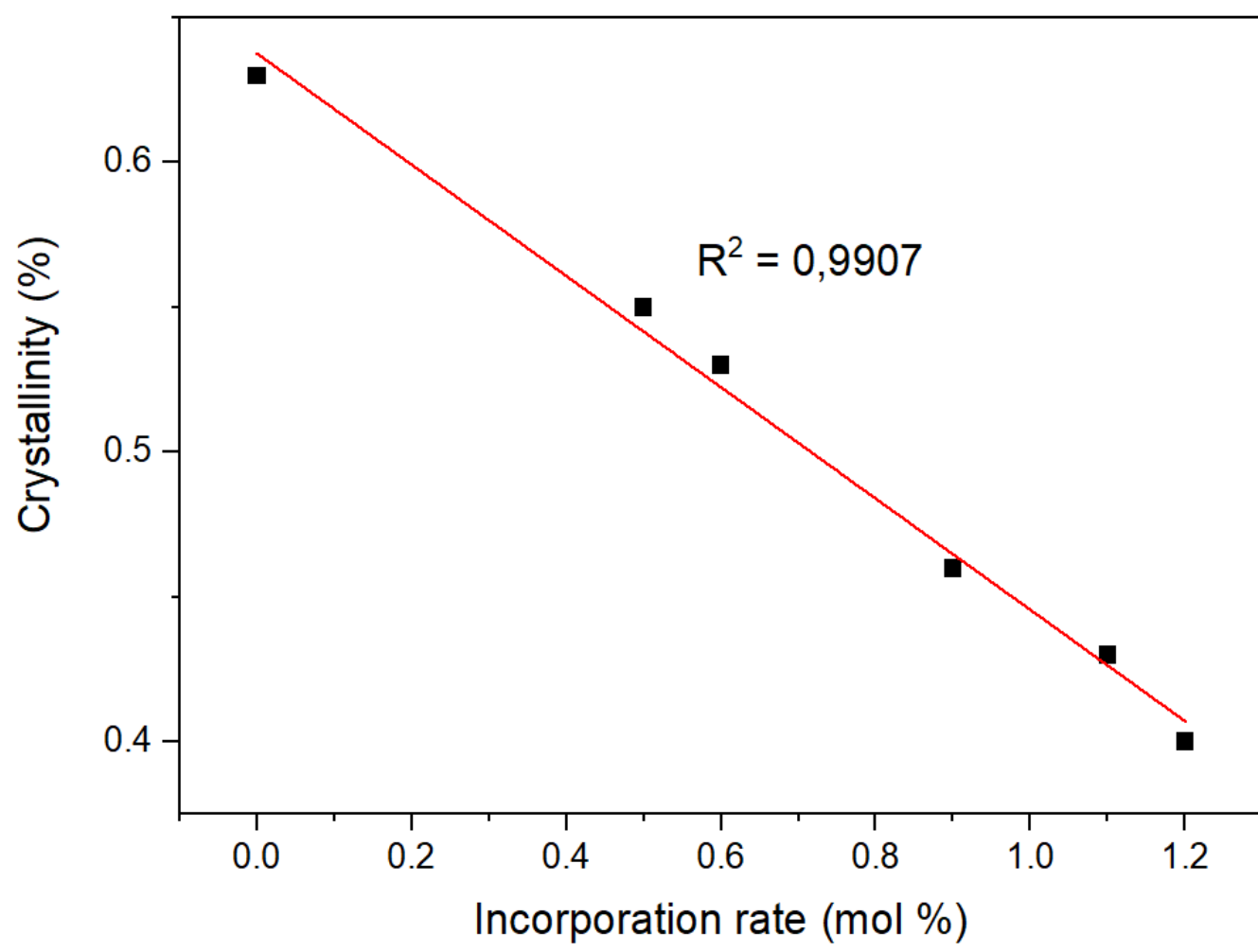


- Additive-tolerant reaction

Optimization made on HDPE

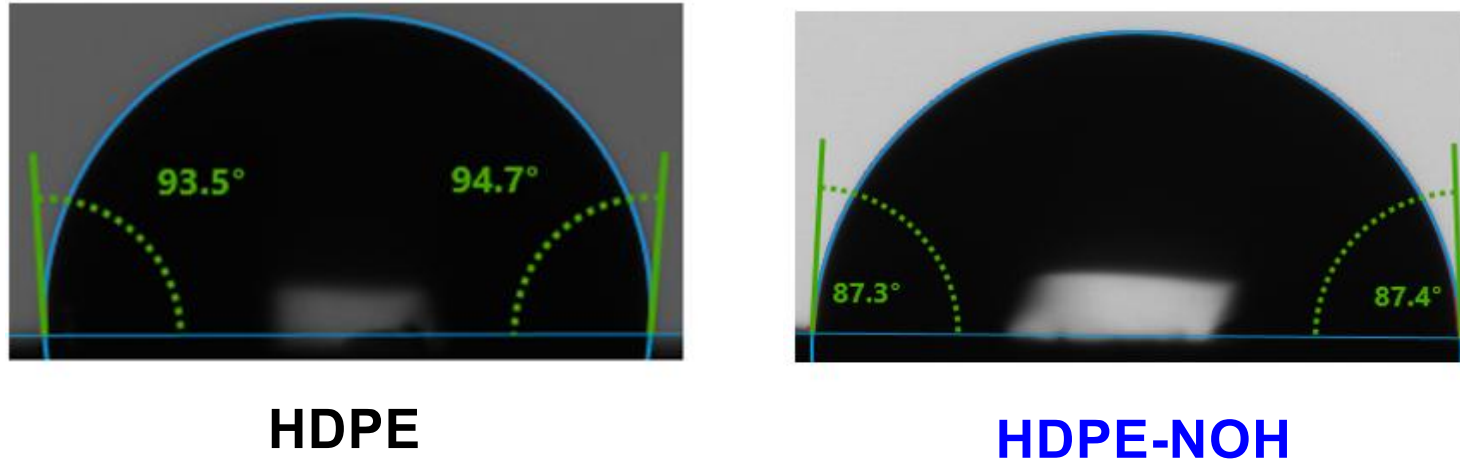
Entry	PT (mol%)	λ (nm)	Incorporation rate (mol%) ^a	Yield (%) ^b
1	-	370	0.3	97
2	-	427	NR	98
3	1	370	0.6	98
4	1	427	0.6	99
5	0.2	370	0.5	Quant.
6	0.5	370	1.3	96
7	0.5	390	1.2	Quant
8	0.5	427	1.4	99

Thermal Properties



- Crystallinity decreases linearly after reaction

Surface properties

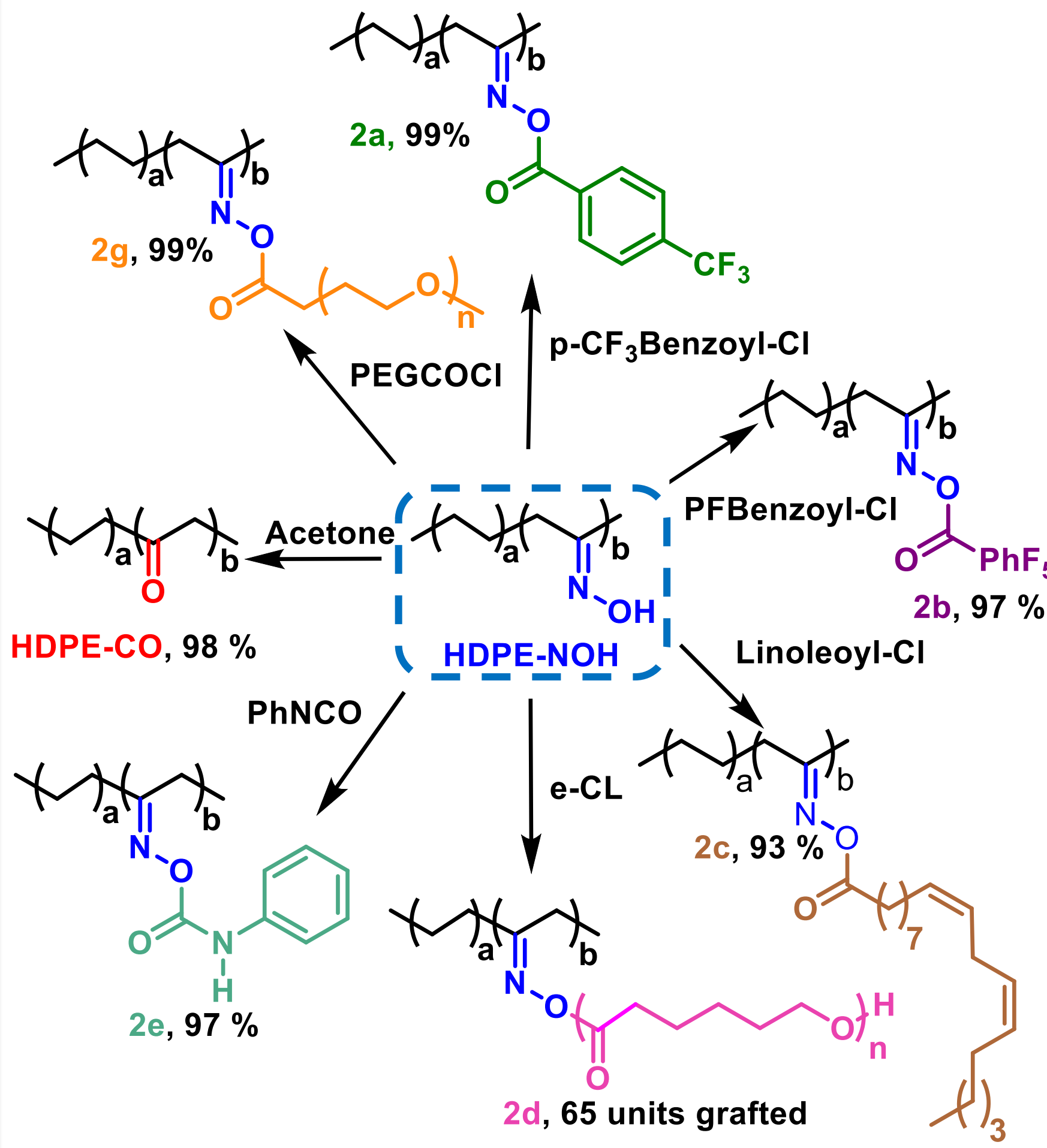


- PE hydrophobicity decreases after modification

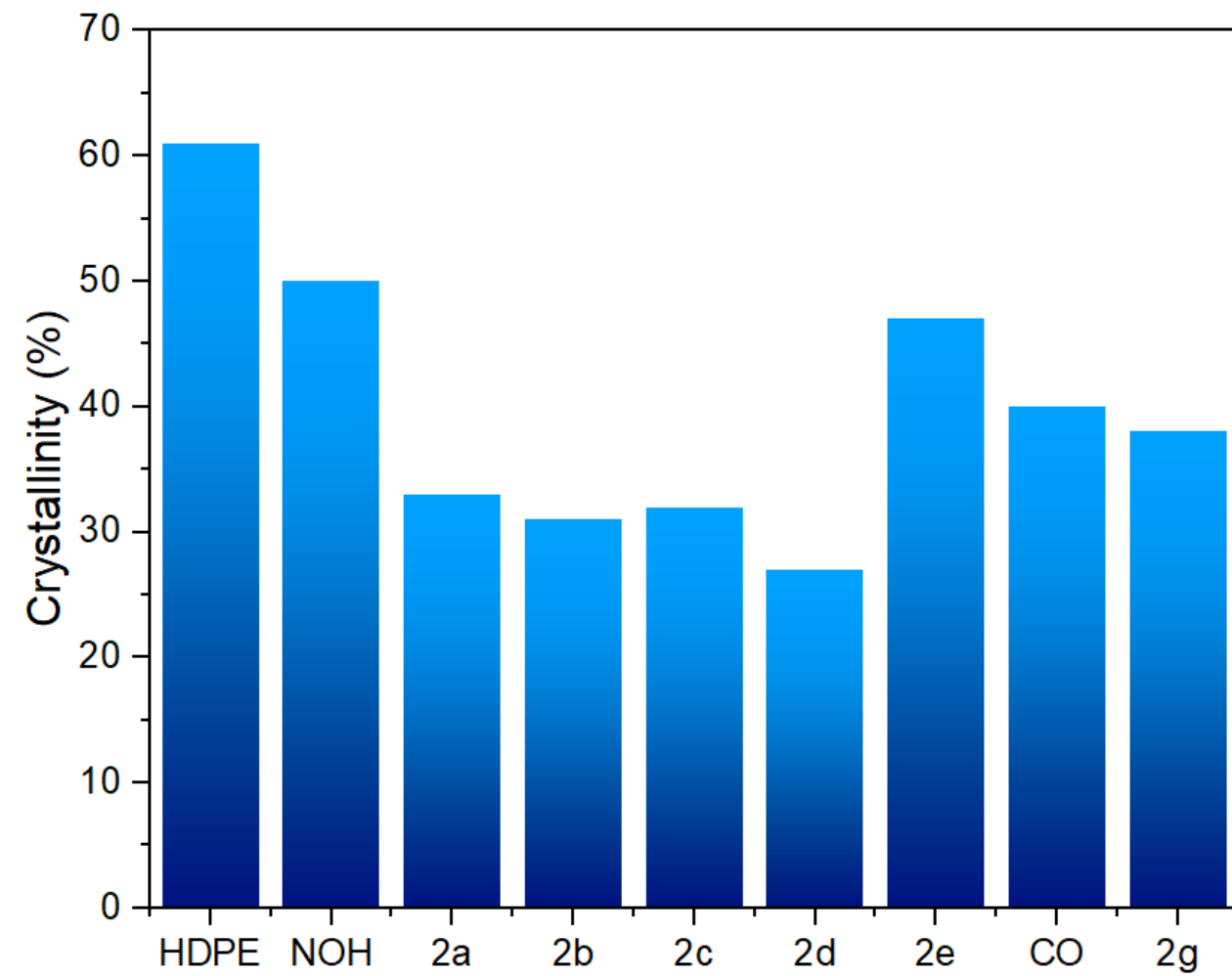
- ✓ Metal Free Selective C-H activation process
- ✓ Direct access to ketoxime and keto-PE and no side reaction
- ✓ Ketoxime reactivity can be used to tune properties

VALORIZATION

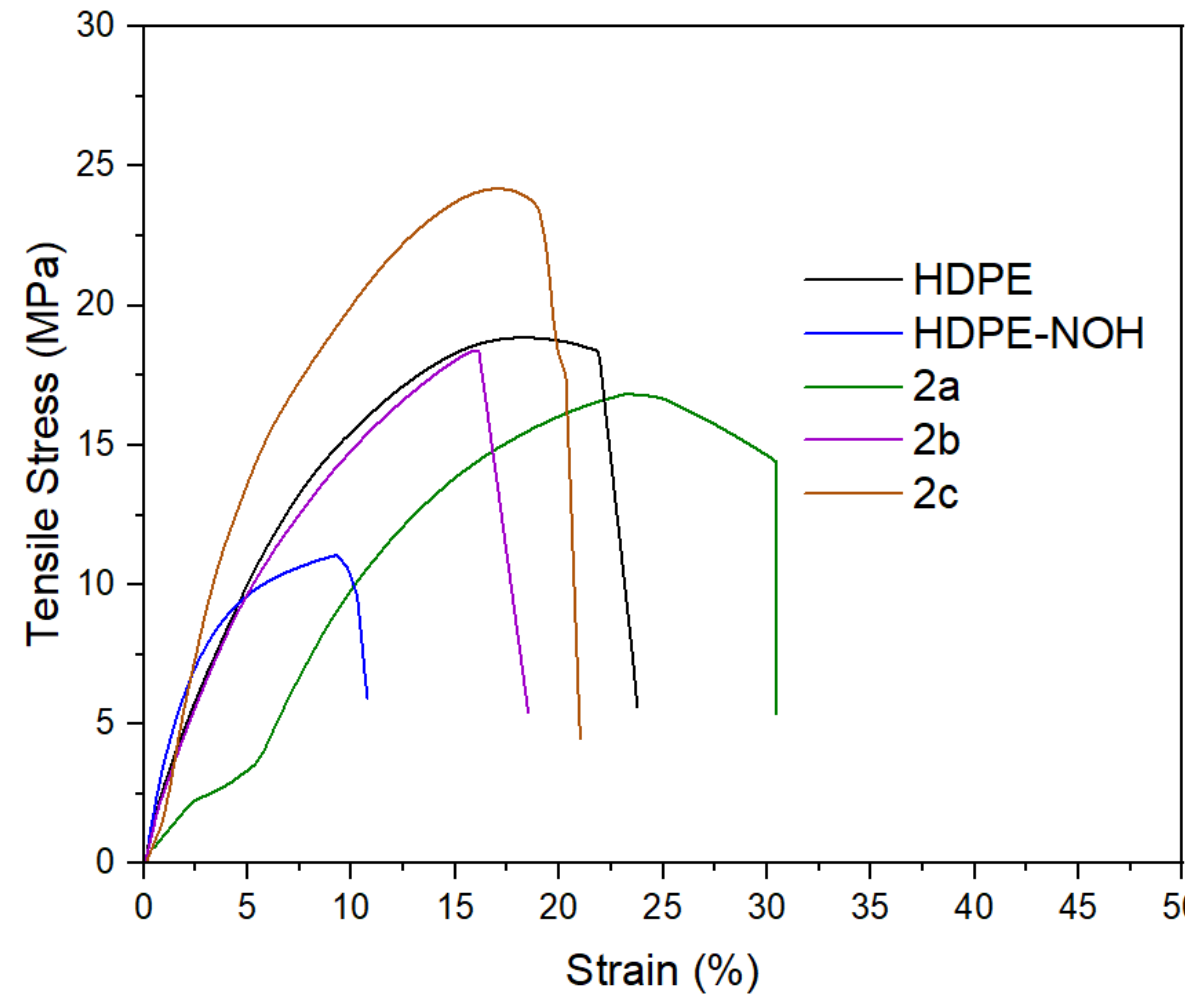
- Post-Functionalization :



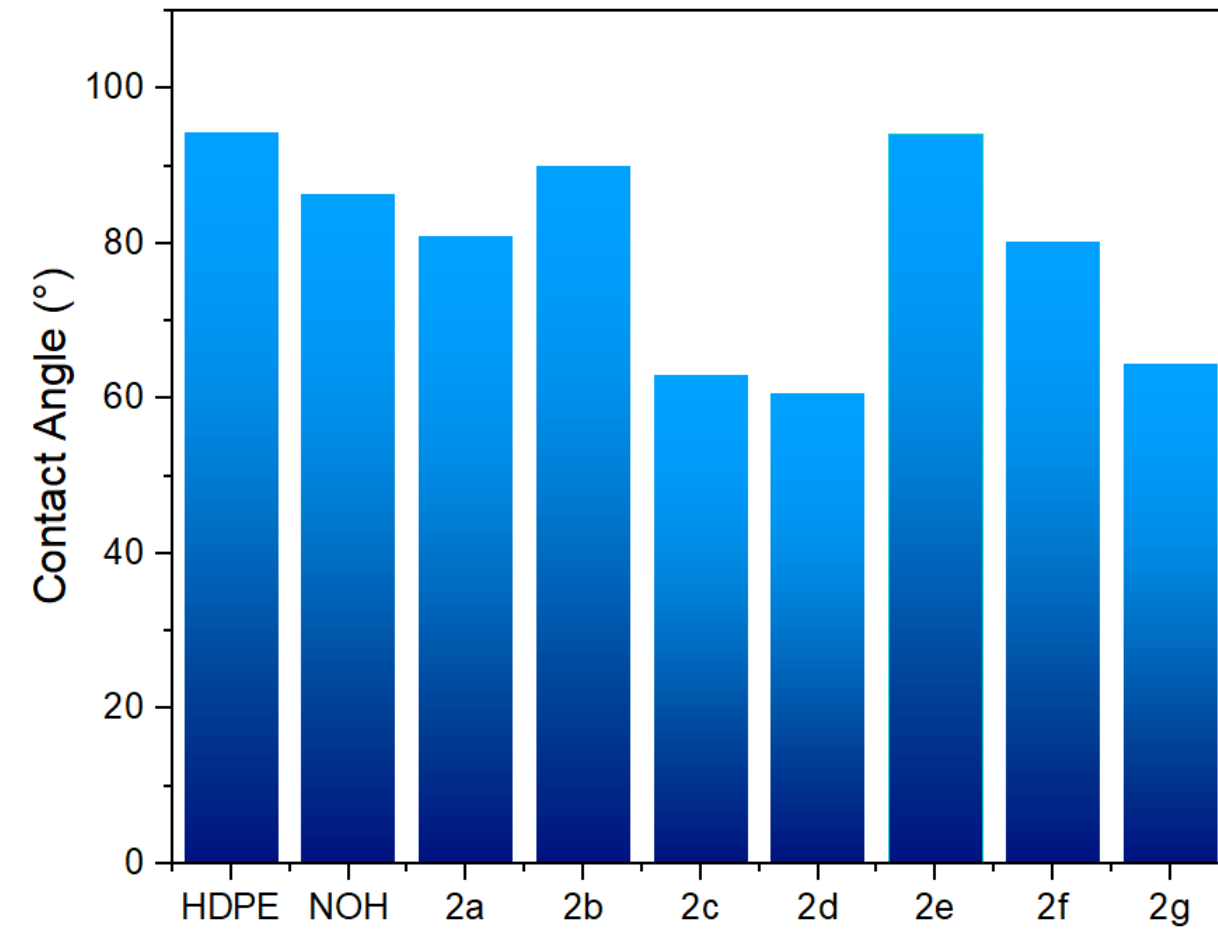
Thermal Properties



Bulk Properties



Surface properties



- ✓ High added-value materials
- ✓ Improvement of Compatibility and Wettability
- ✓ Modification of thermal, surface and mechanical properties.

CONCLUSION AND PERSPECTIVES

- A photo-nitrosation reaction enables oxime grafting (~1.4 mol%) onto PE, notably modifying its surface, mechanical and thermal properties.
- Oximes open post-functionalization routes and facilitate recycling by breaking bonds into reusable oxidized fragments.
- This method is chemoselective, metal-free, and applicable on a gram scale.

REFERENCES

- [1] Hartwig, J. F. *et al.*, *J. Am. Chem. Soc.* **2023**, *145*, 21527–21537.
- [2] Tang, Y. *et al.*, *Prog. Polym. Sci.* **2023**, *143*, 101713.
- [3] Alexanian, E. J.; Leibfarth, F. *et al.*, *Science* **2022**, *375*, 545–550.
- [4] Landais, Y. Taton, D. Robert, F. Cluzeau, L. Patent FR2307794, **2025**.
- [5] Cluzeau L. *et al.*, soon to be submitted, **2025**.