# POLYPHOSPHOESTER ELASTOMERS: A SYNTHETIC INVESTIGATION TOWARDS IMPROVED ELASTIC CAPACITIES

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## INTRODUCTION

Among numerous possible applications of elastomers, the biomedical field is one of the most demanding regarding physical properties. In this work, a rising class of degradable polymers is being studied: **polyphosphoesters**. This type of polymers is promising for the biomedical field thanks to its proven **biocompatibility** and **degradability**. Though, polyphosphoester networks do not exhibit elastomer properties yet. The aim of this project was to improve the elongation capacity of polyphosphoester networks to enrich the features this class of polymers can offer.

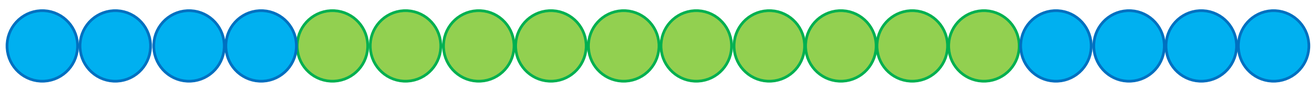
## STRATEGIES

Our strategies are based on the Phantom model which predicts the elastic modulus of chemically crosslinked networks, depending of two factors : molar mass between crosslinks, and the functionality of the nodes i.e. the amount of chains that participate in a linkage.

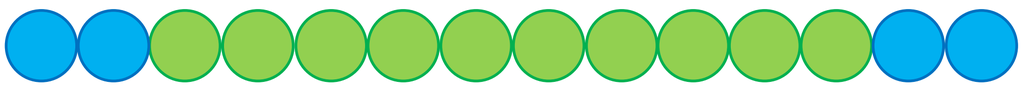
Blocks size variation ⟸ $E = \frac{3RTd}{M_c}\left(1 - \frac{2}{f}\right)$ ⟹ Modification of the polymer backbone

Random copolymer

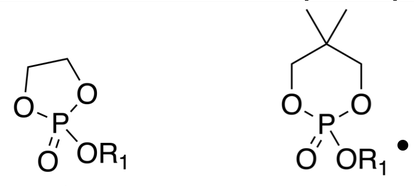
Organised triblock



Blocks length variation



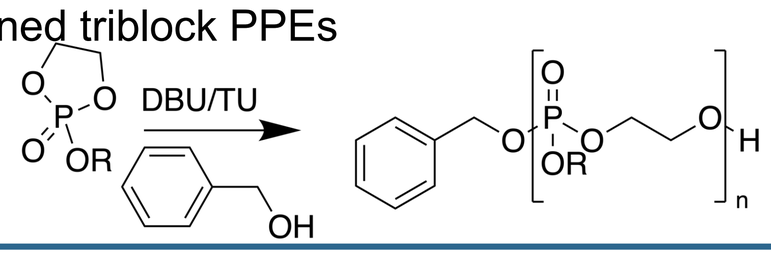
ROP of 6-membered phosphate ring monomers



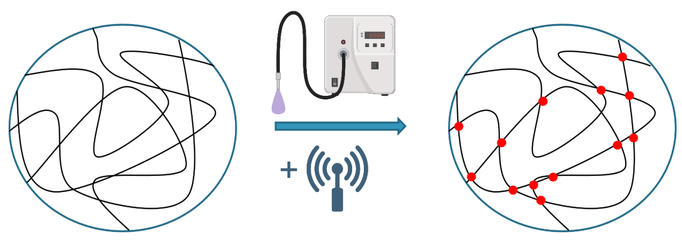
- MM ⇧ with the same DP
- Backbone stiffness

## EXPERIMENTAL

- **Organocatalyzed ROP** for the synthesis of well-defined triblock PPEs




- **UV crosslinking** at 365 nm with a photoinitiator (LAP)



- **Network characterization** : swelling tests, rheology, tensile tests, degradation studies

## RESULTS

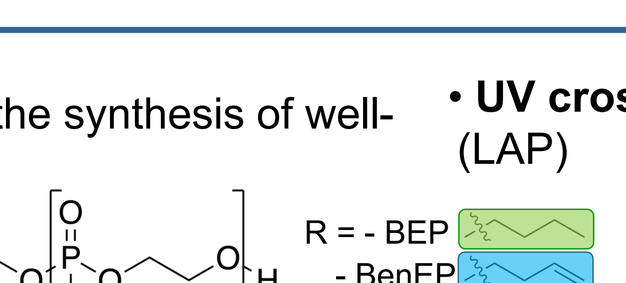
### Effect of the crosslinking density and crosslinking conditions on the mechanical properties

1) Mechanical screening of polymers with different architectures

| Polymer composition | Gel point [min] | G'$_p$ [kPa] | E [kPa] |
|---|---|---|---|
| 5-130-5 | 5.9 | 105 | 170 |
| 10-130-10 | 1.4 | 188 | 390 |
| 20-130-20 | 1.4 | 530 | 980 |
| 1-130-1* | 0.4 | 26 | 0.04 |

*acrylic group

Effect of external blocks length (copolymer functionality) on tensile properties



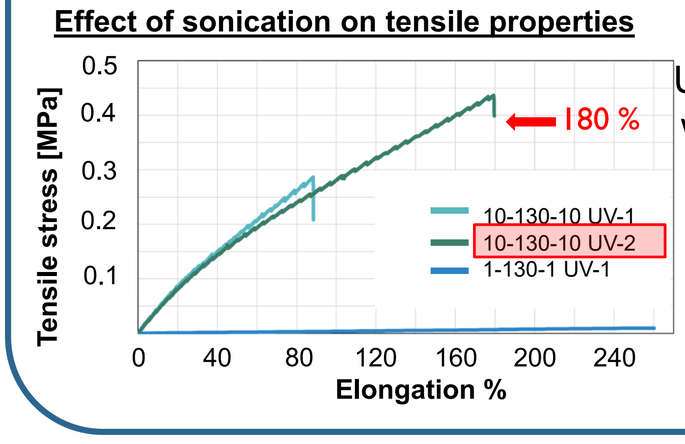

2) **Sonication** as parameter enhancing mechanical properties

Crosslinking conditions :
- UV-1: dry state irradiation
- UV-2 : in MeOH solution irradiation in ultrasonic bath

Solubilisation of the polymer in MeOH decreases entanglements

=> **Mc** ↑, $\varepsilon_{max}$↑

Effect of sonication on tensile properties



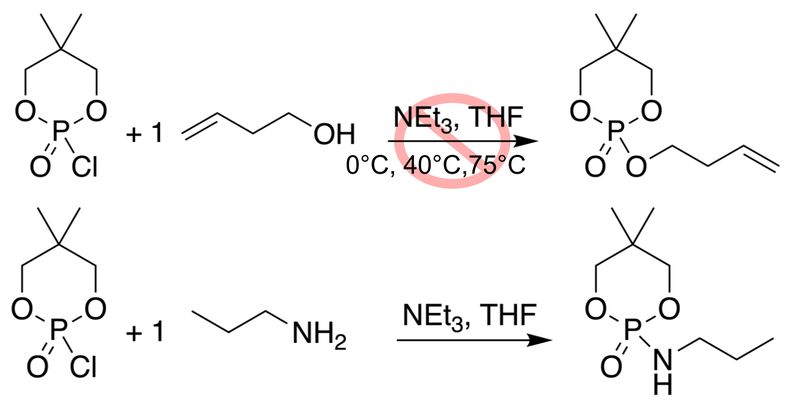

Ultrasound brings an energy boost, which leads to increased reactivity of BenEP units unsaturation

=> **f** ↑, **E** ↑

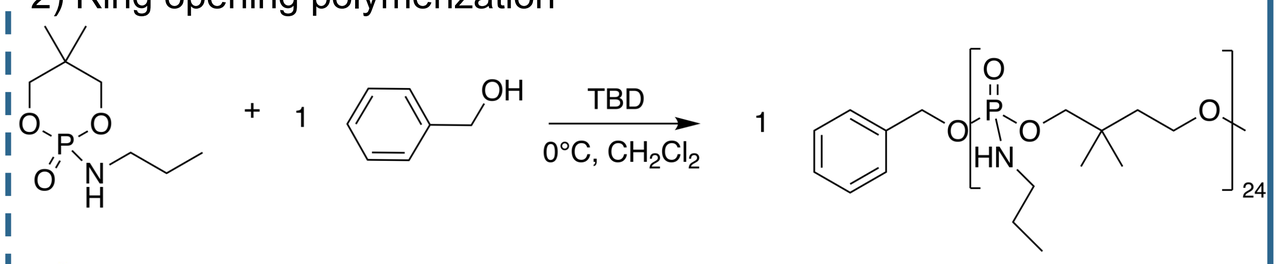
**Strain hysteresis experiments further confirmed the elastic character of the networks**

### Exploring a new synthetic pathway to increase stiffness along the polymer backbone

1) Monomer synthesis starting from commercial DPPC



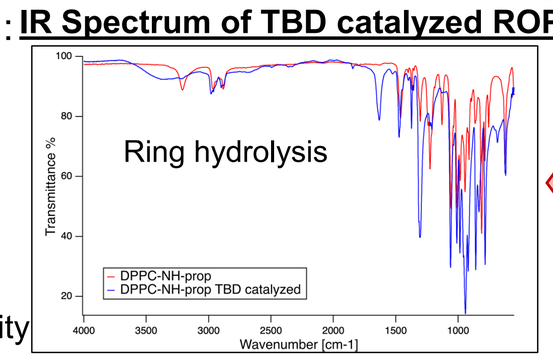

2) Ring opening polymerization

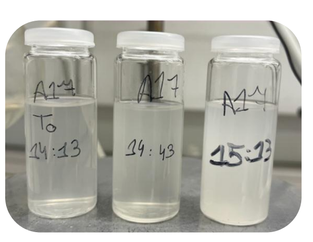



Precipitation in diethyl ether

Workarounds : **IR Spectrum of TBD catalyzed ROP**

- **Stronger** organic bases
- Perform **computational study** to understand compound reactivity



## CONCLUSIONS & OUTCOME

In this work, we report the **first polyphosphoester elastomer with a maximum elongation at break reaching 180%** where the last published elongation did not exceed 15%. We further established relationships between the microstructure of the polymer chains and their mechanical properties, such as Young's modulus and ultimate elongation. We demonstrated the modularity of PPEs mechanical properties, which rises their attractivity for applications in the biomedical field, such as tissue engineering. Regarding the polymerization of six-membered monomers, the preliminary experiments exhibited lower reactivity than that of five-membered counterparts. Nevertheless, we believe that with optimized catalytic systems, the polymerization of such monomers is achievable.

## REFERENCES

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2. Riva et al. *Biomacromolecules* **2020**, 21(2), 349–355.
3. Rheinberger et al. *European Polymer Journal* **2023**, *190*, 111999.
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## ACKNOWLEDGMENTS

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