

# Développement d'un PLA ignifugé par polymérisation par ouverture de cycle et extrusion réactive.

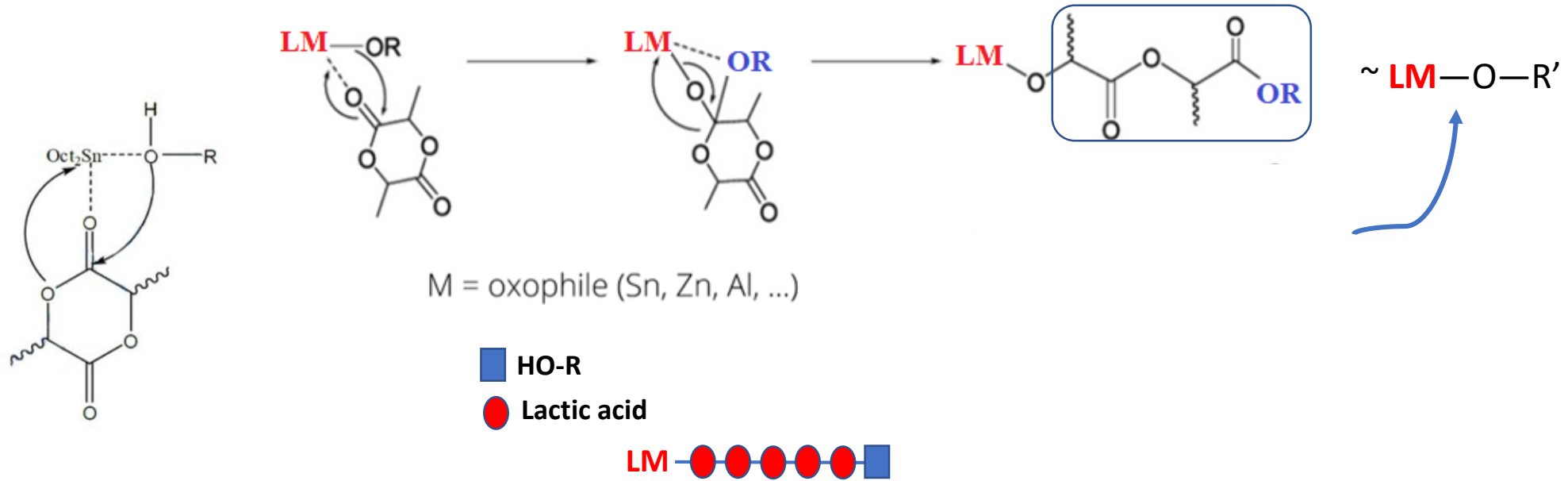
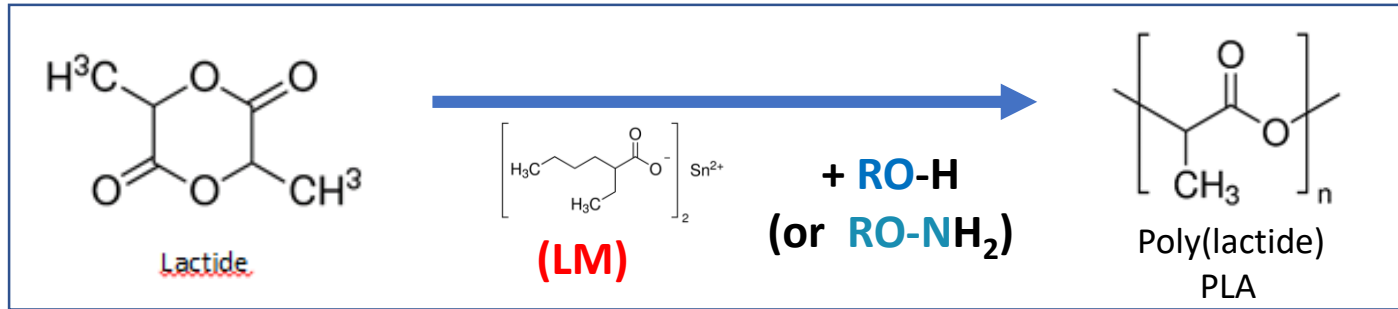
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□ Ring-opening polymerization of lactide

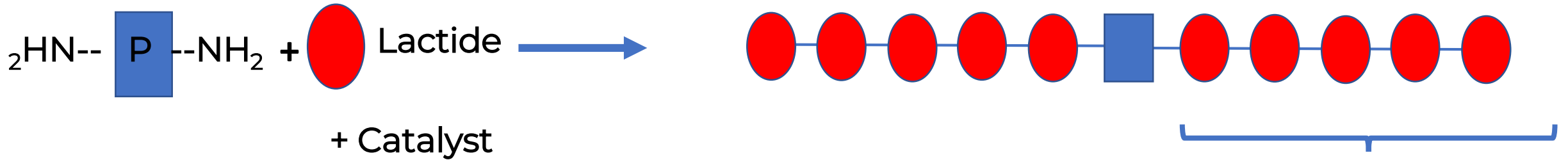


# Preparation of inherently flame-retardant polylactide

## Using reactive pathway to develop inherent FR PLA

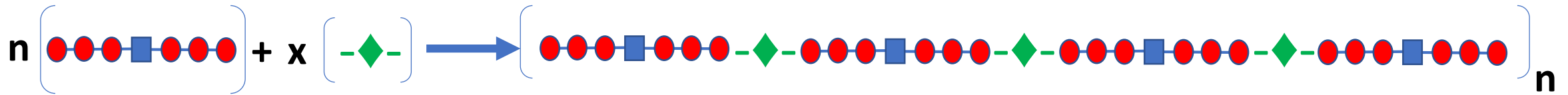
- Adding P into PLA chain : 2 steps

### 1) *First step:* Preparation of phosphorylated PLA oligomers

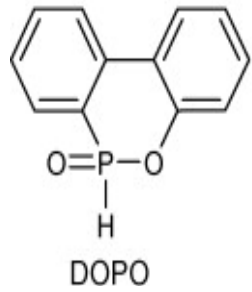


“L” could be controlled

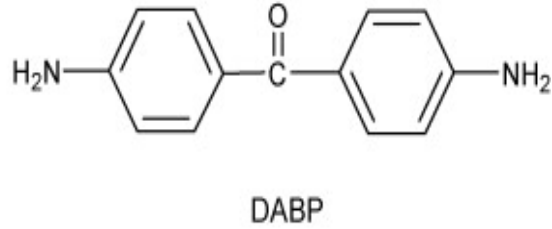
### 2) *Second step:* Chain extension



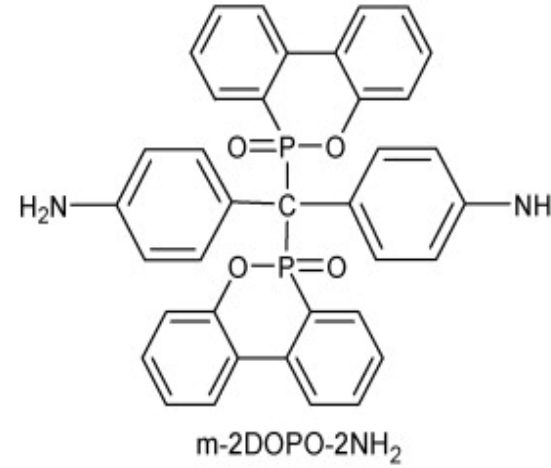
# Preparation of bifunctional P-based initiator



9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)



4,4'-Diaminobenzophenone (DABP)

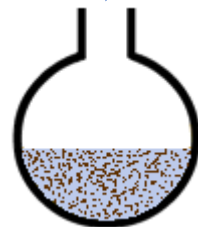


32g DOPO    5,35g DABP



180 °C, 3 h

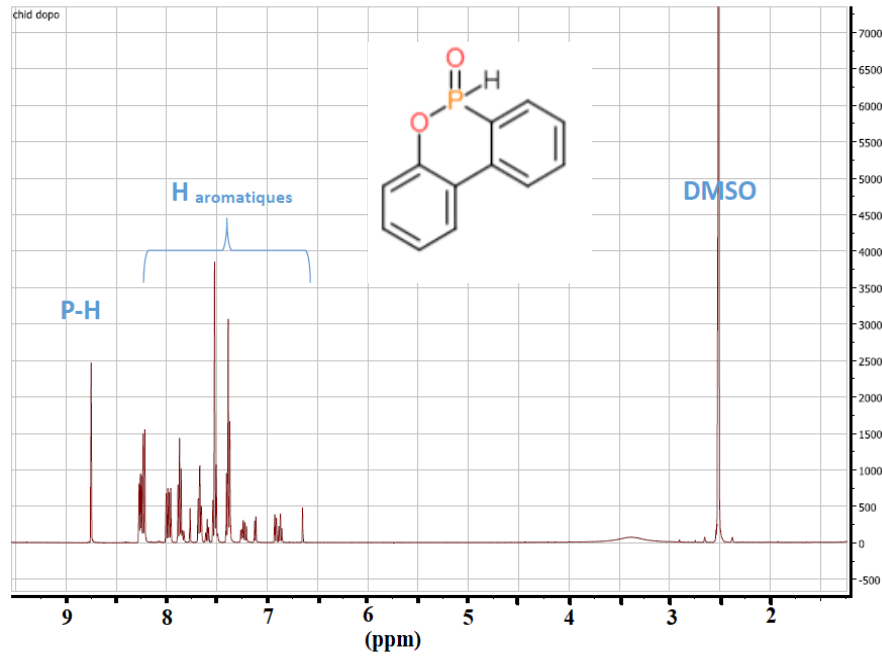
At 100 °C +  
Toluene (150 ml)



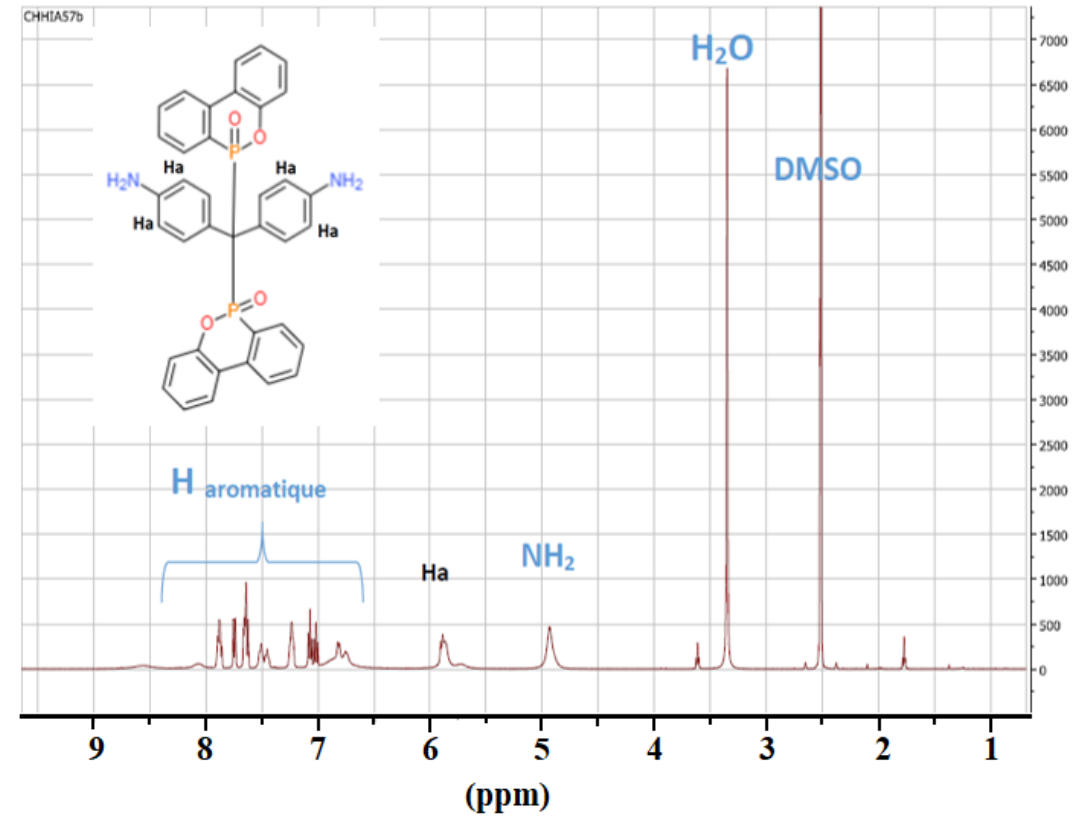
Washings +  
Crystallization with  
THF

→ Yellow Powder

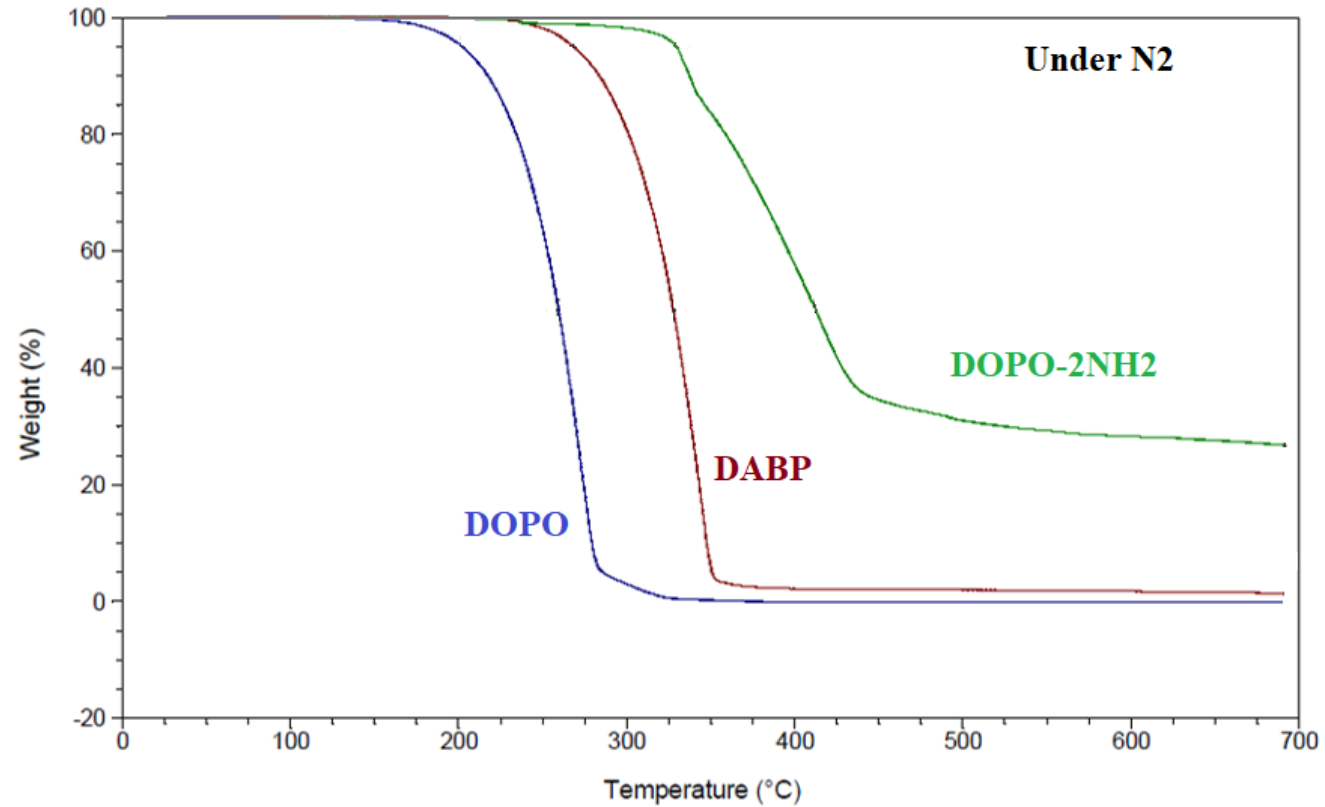
## <sup>1</sup>H NMR



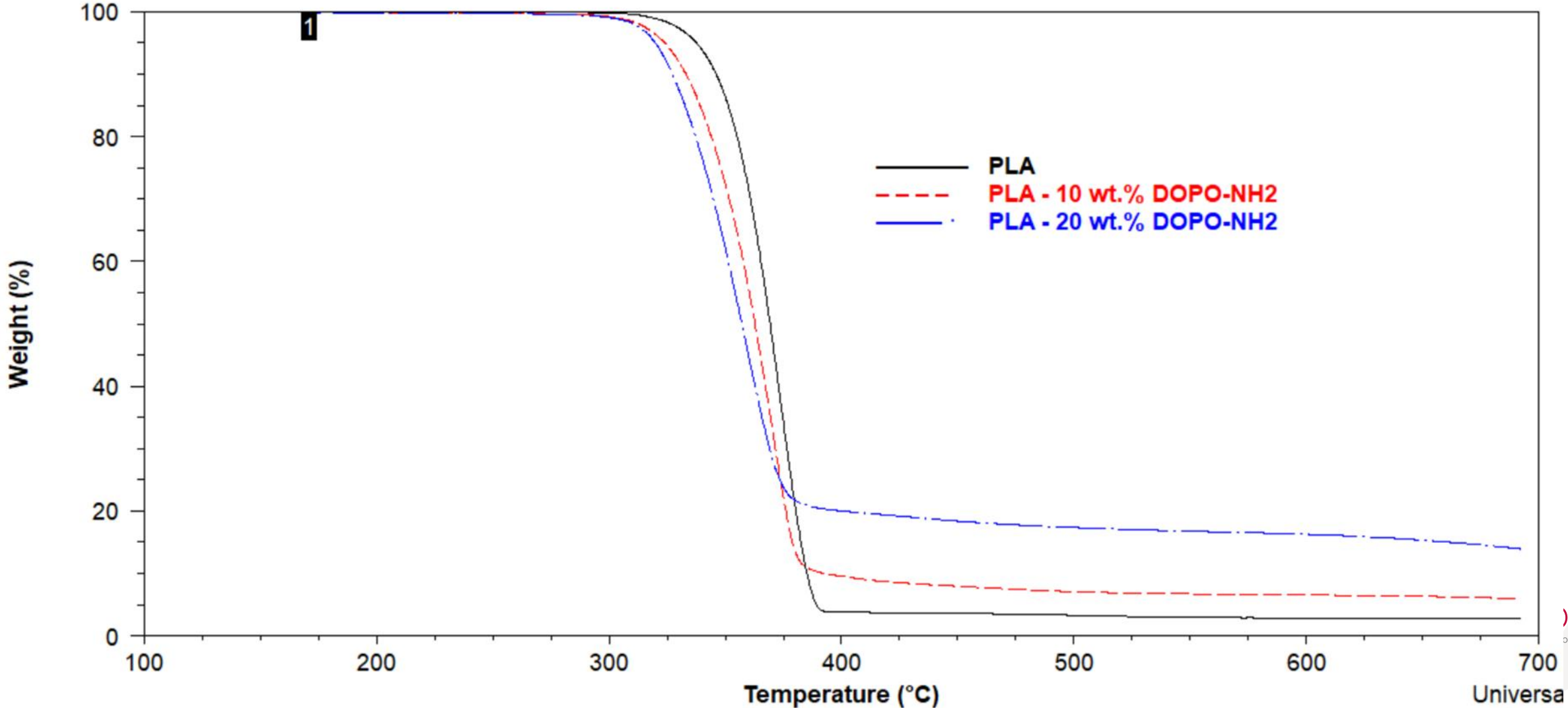
**No P-H peak**



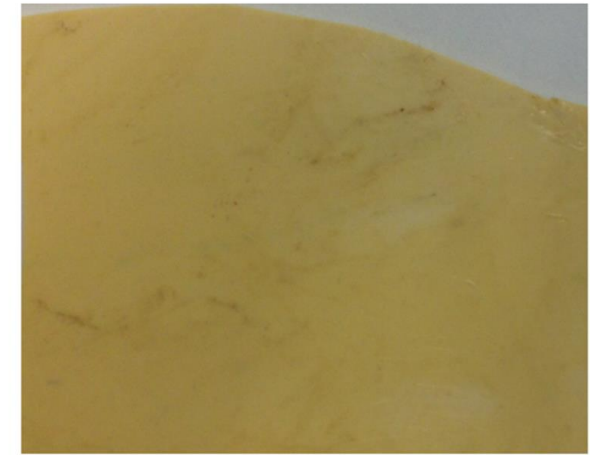
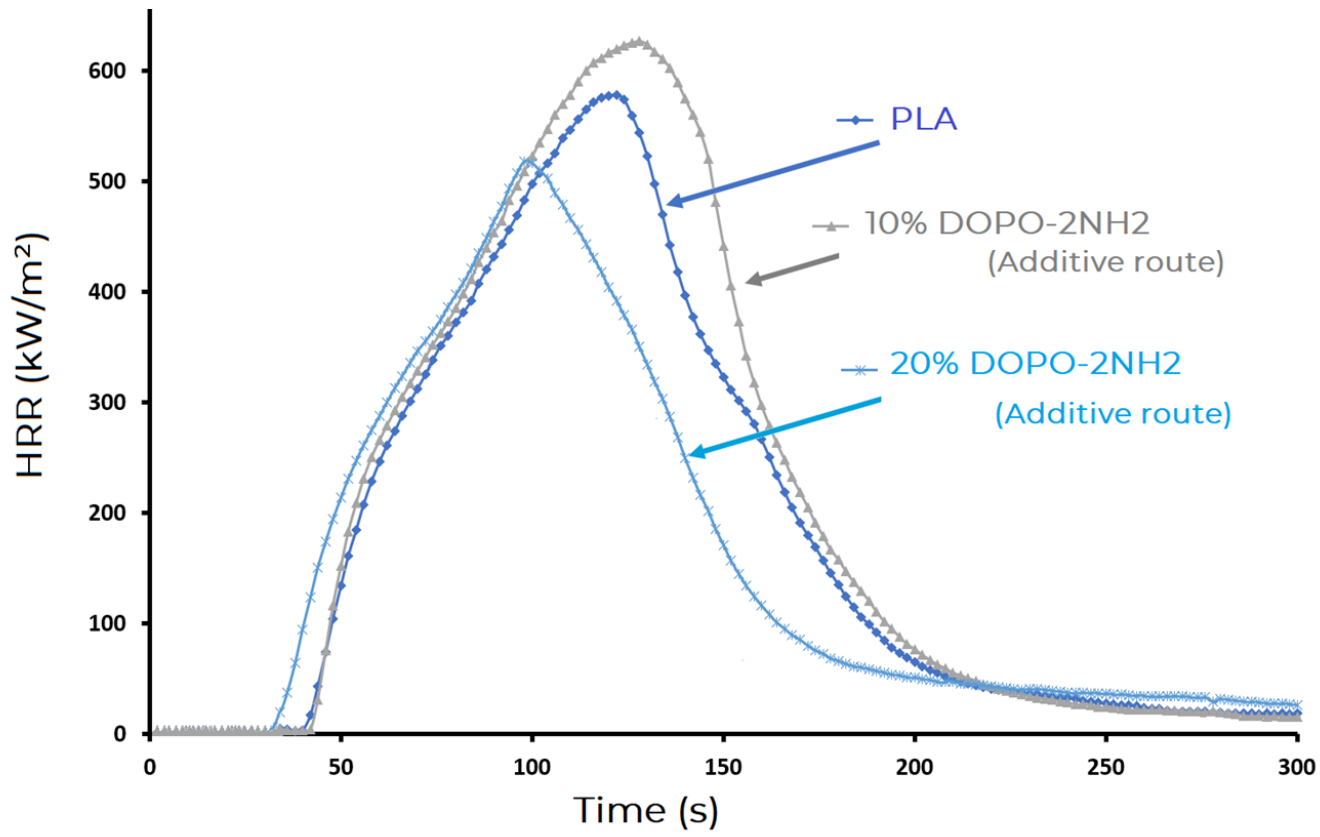
□ TGA : under N<sub>2</sub>, 20°C/min



☐ TGA : under N<sub>2</sub>, 20°C/min



☐ Cone calorimeter (35 kW/m<sup>2</sup>)

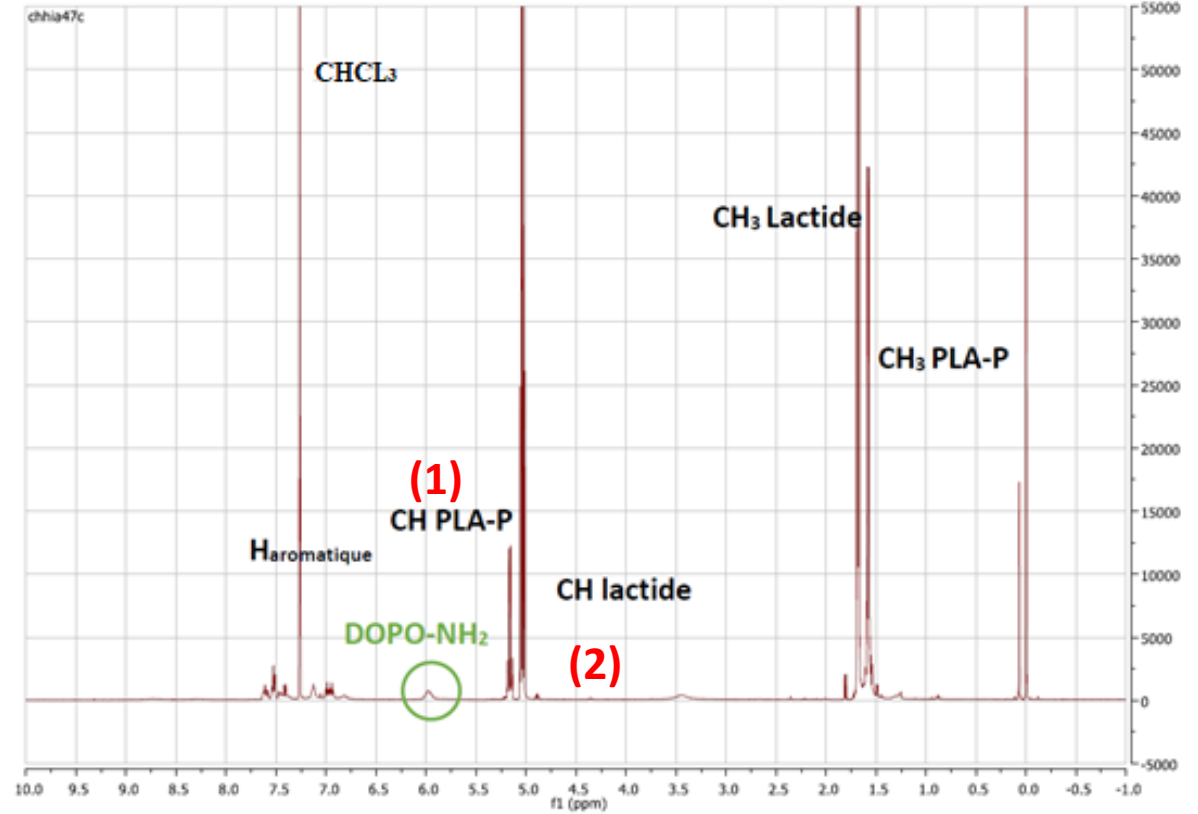
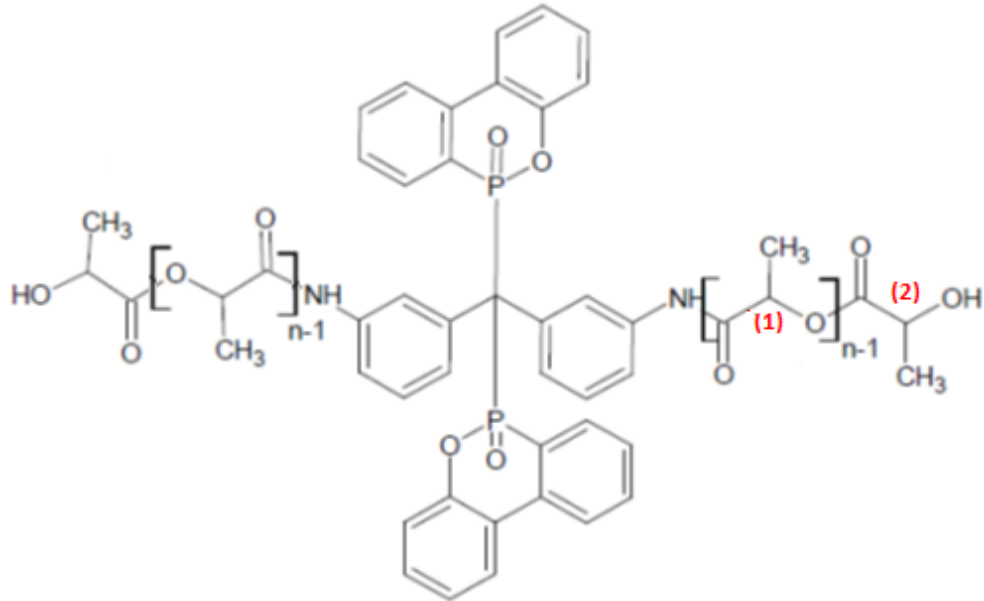


**PLA + 20 wt.% DOPO-diamine**



# Preparation of Phosphorylated PLA oligomers

- At **100°C**
  - Target Degree of Polymerization (DP = 30)
    - L-Lactide : 1g
    - Initiator/Catalyst ratio : 1 NH<sub>2</sub> for 1/200 Sn(Oc)



Sample	Target DP	Obtained DP	Residual DOPO-NH <sub>2</sub> (%)
1	30	80	80

We obtained:

- PLA – DOPO NH<sub>2</sub>
- DOPO NH<sub>2</sub>
- Lactide

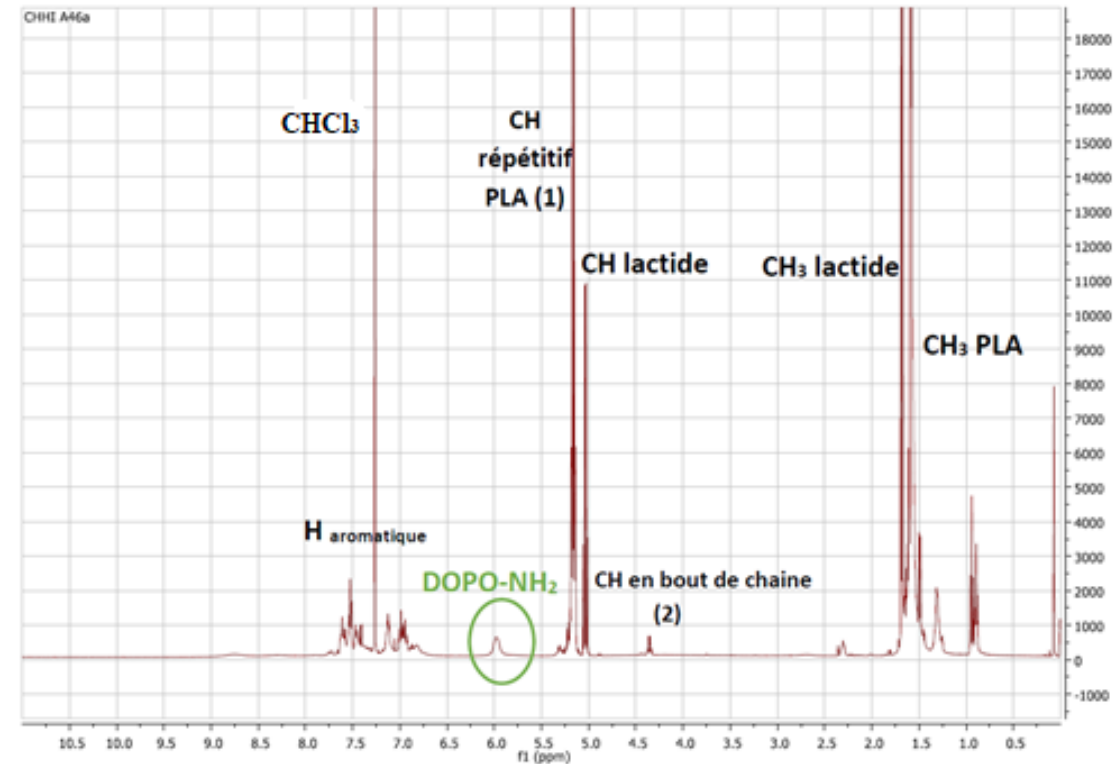
→ ↑ Temperature

# Preparation of Phosphorylated PLA oligomers

- At **150°C**  
→ Target Degree of Polymerization (DP = 10; 20 & 30)



Sample	Target DP	Obtained DP	Residual DOPO-NH <sub>2</sub> (%)
1	10	42	76
2	20	70	53
3	30	62	56

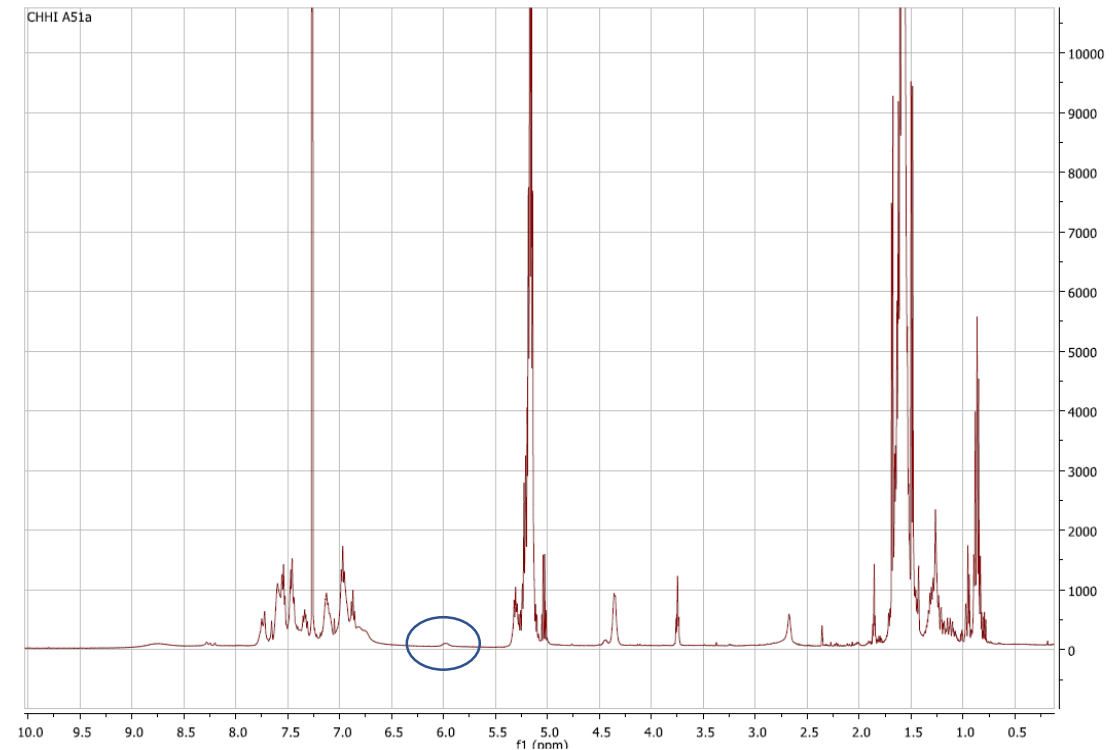


# Preparation of Phosphorylated PLA oligomers

□ At 180°C

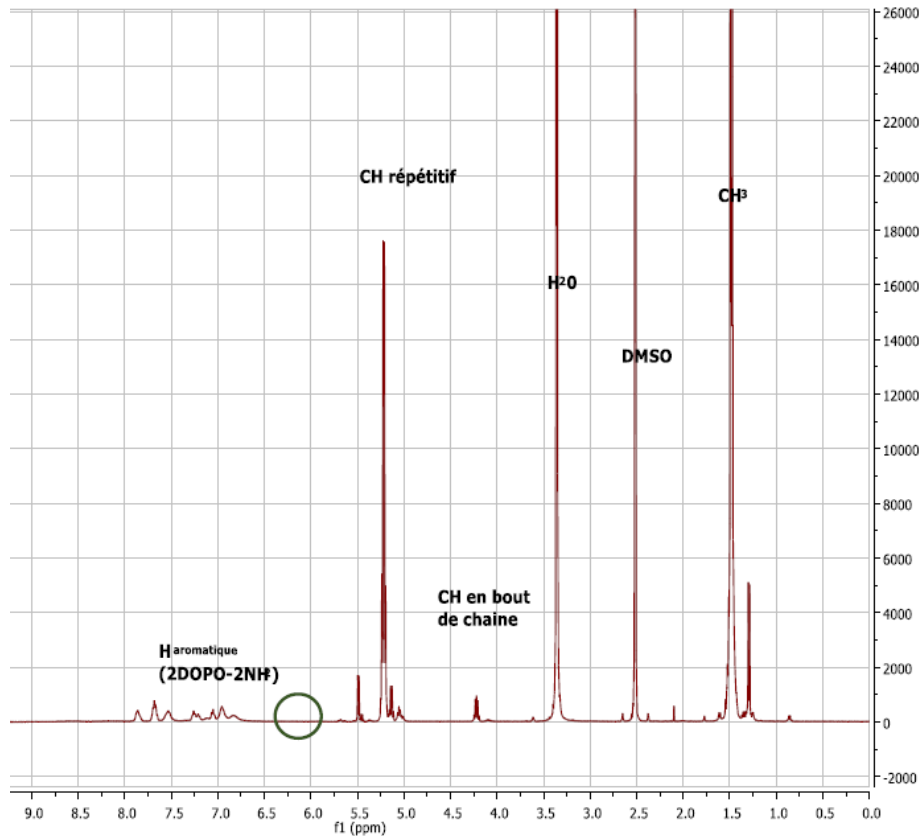


Sample	Target DP	Obtained DP	Residual DOPO-NH <sub>2</sub> (%)
1	10	14	11
2	20	16	12
3	30	32	15



**Using reactor** of 250ml (under N<sub>2</sub> / 4 bars).

- 1st: Initiator (DOPO-2NH<sub>2</sub>) + L-lactide during 15 minutes et 180°C
- 2<sup>nd</sup>: Introduction of catalysis Sn(Oct)<sub>2</sub>.
  - + 180°C during 50 minutes under mechanical stirring at 50 rpm.
  - + Solubilisation in THF followed by precipitation in cold methanol.

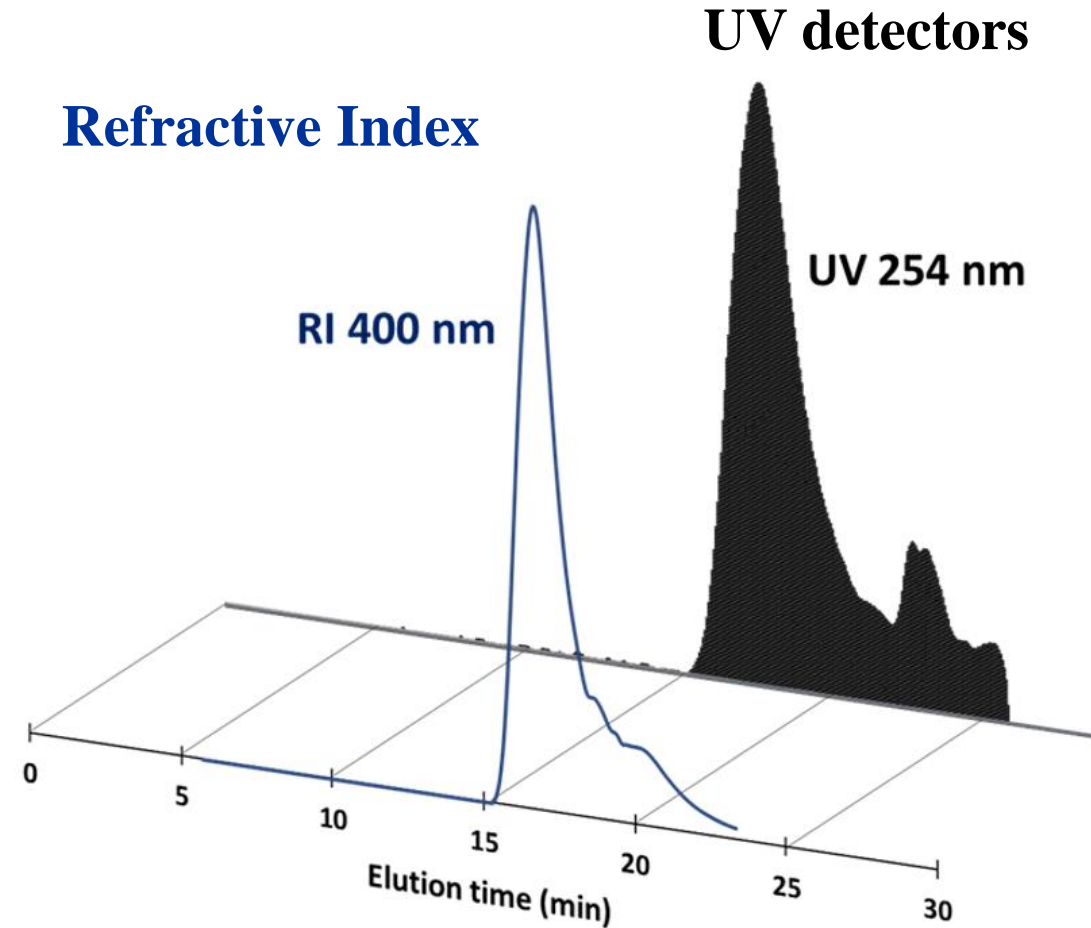


Sample	Obtained DP	Obtained MW (g/mol)	Residual DOPO-NH <sub>2</sub> (%)
PLA-P	15	2786	0

## □ Size Exclusion Chromatography (SEC)

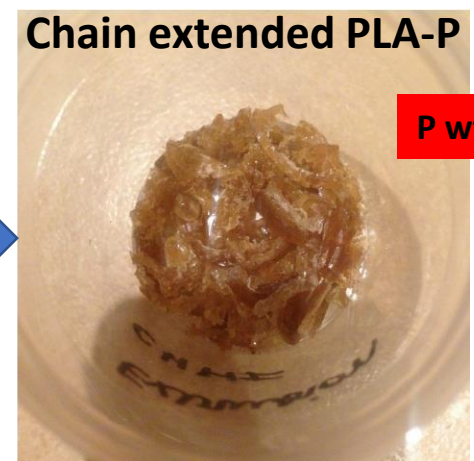
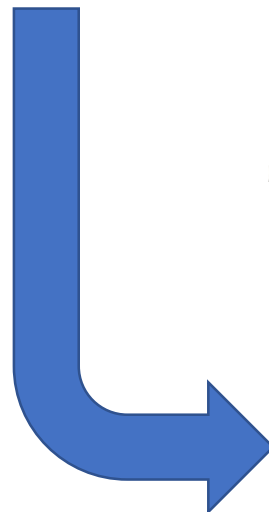
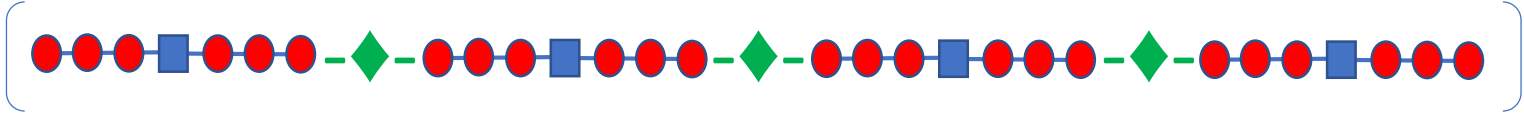
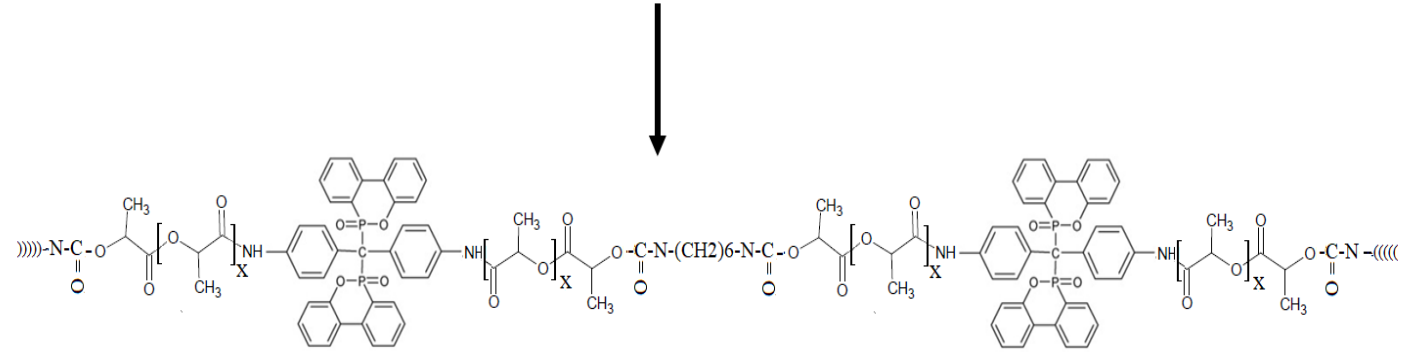
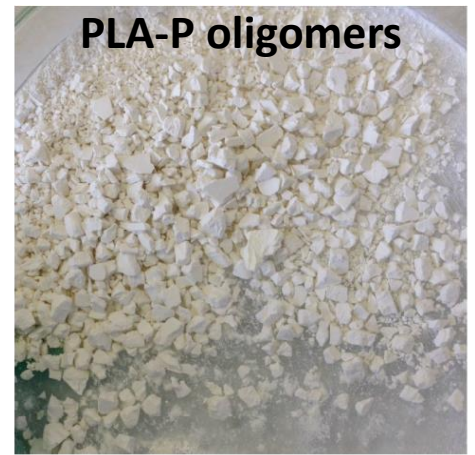
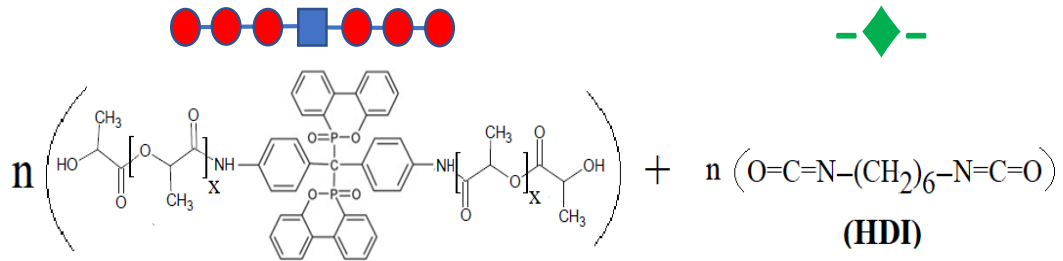
→  $M_n = 2\,700 \text{ g}\cdot\text{mol}^{-1}$

→ DOPO is distributed throughout the sample.



# Chain extension of Phosphorylated PLA oligomers

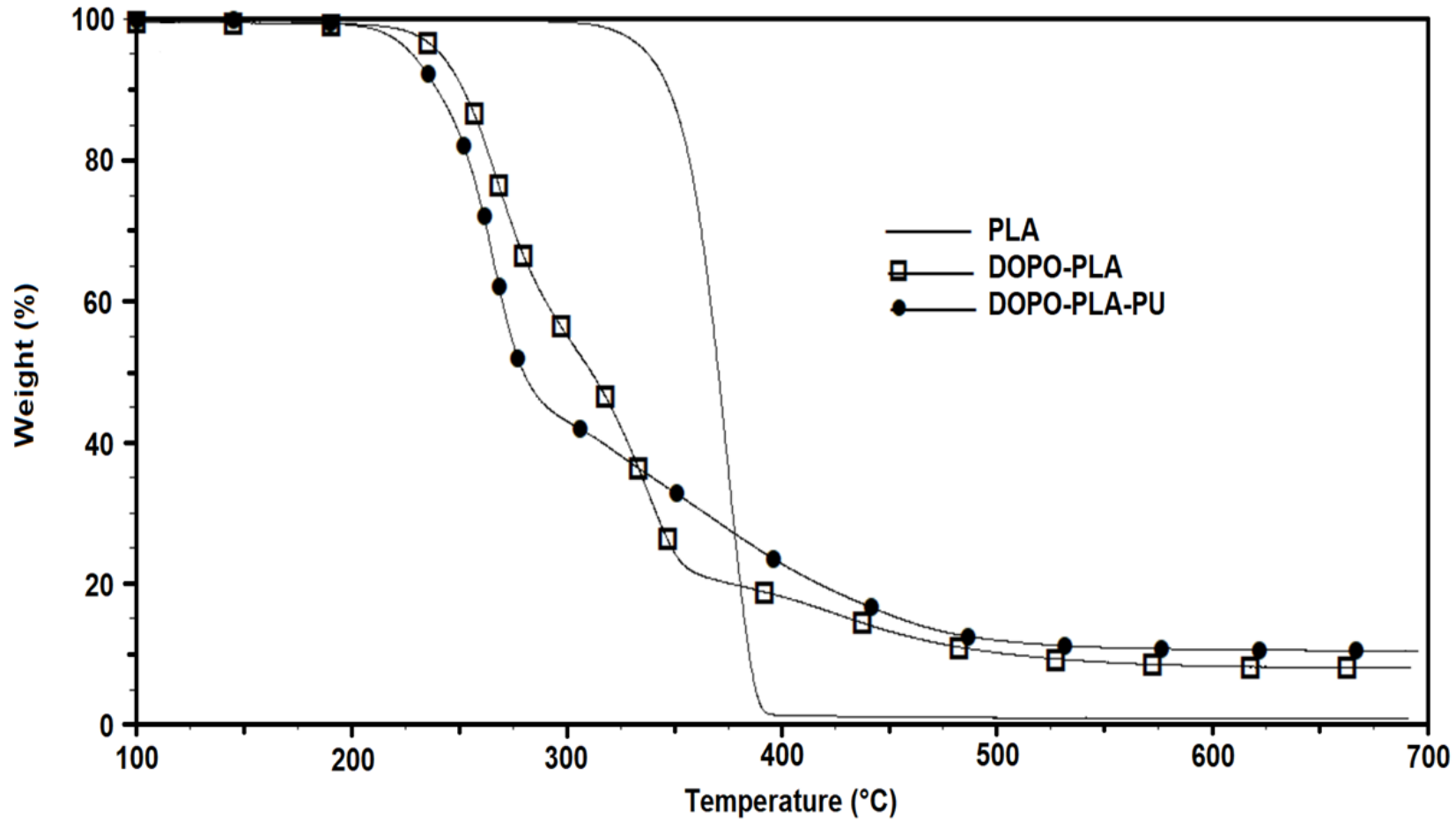
- Chain extension using Hexamethylene diisocyanate (HDI).
- Equimolar ratio between PLA-P oligomers and HDI.
- DSM mini-extruder at 160°C, during 1 hour 30 at 30 rpm.



**P wt.% = 4%**

# Chain extension of Phosphorylated PLA oligomers

□ Thermal stability, under N<sub>2</sub> (20°C/min)

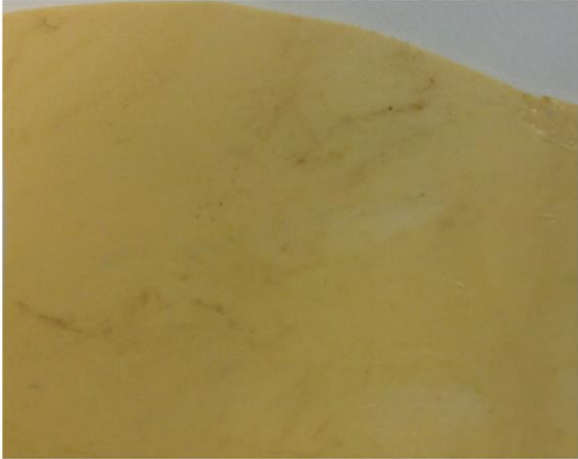


# Incorporation of phosphorylated PLA into PLA

Films (thickness of ca. 0.8 mm)

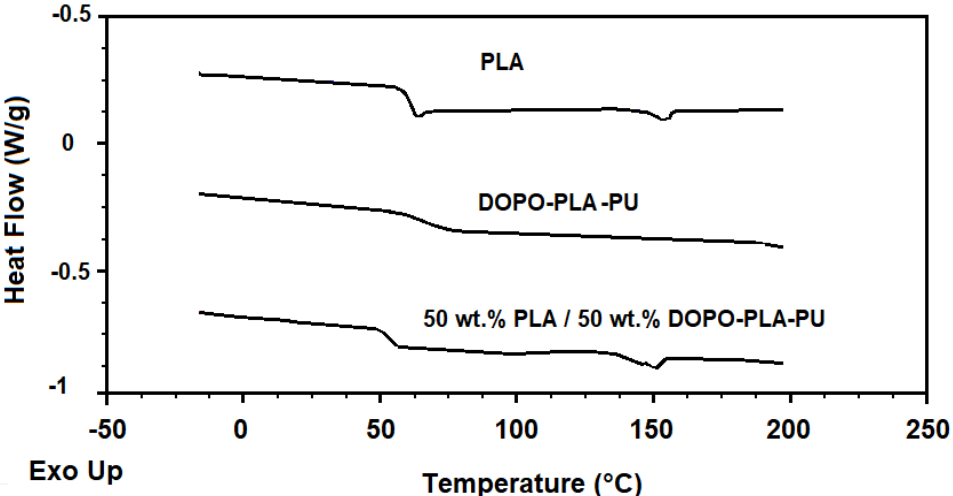


DOPO-PLA-PU



PLA + 20 wt.% DOPO-diamine

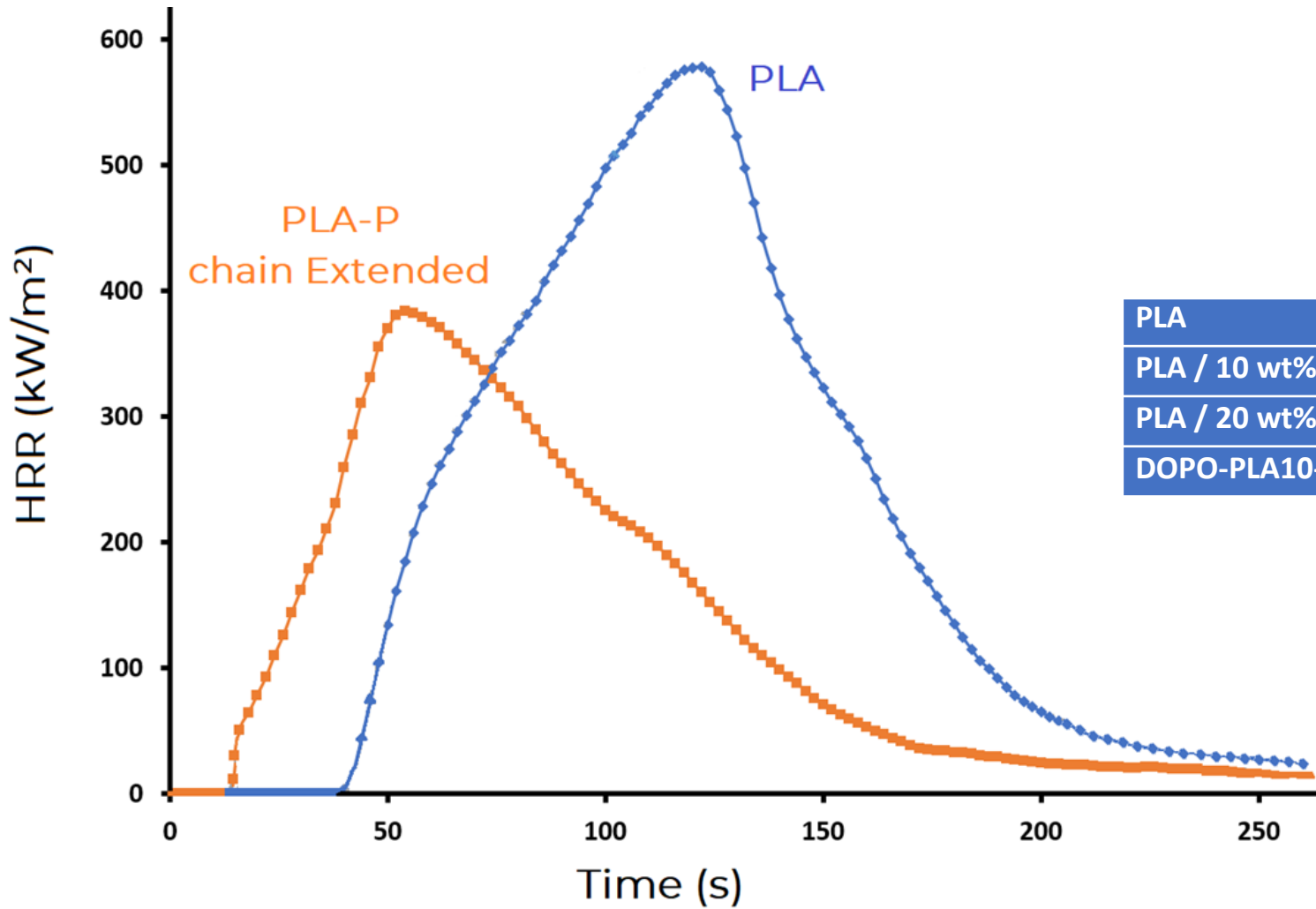
Differential scanning calorimetry (DSC)



Sample	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)
PLA	60	154	2
DOPO-PLA-PU	60.5	-	-
50% DOPO-PLA-PU/50% PLA	50.5	150	3



**☐ Cone calorimeter (35 kW/m<sup>2</sup>)**



	TTI (s)	pHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
PLA	40	580	54
PLA / 10 wt% DOPO-NH <sub>2</sub>	42	620	61.7
PLA / 20 wt% DOPO-NH <sub>2</sub>	34	520	51
DOPO-PLA10-PU	16	380	34.5

## Fire properties



- 😊 PLA ROP polymerization, using DOPO / DABP is suitable way for the production of well controllable P-PLA oligomers at 180 °C
- 😊 REX enable increasing the Mn of P-PLA
  - 😞 Obtained material presents low thermal stability
  - 😊 Higher transparency
- 😊 Flame retardant behavior
  - 😊 Reduction of pHRR
  - 😊 Reduction of THR
  - 😞 Reduction of TTI
- 😊 Phosphorylated PLA could be used as FR additive for PLA
  - 😊 Dripping V0 for 0,8 mm films



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