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European network of FURan based chemicals  
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UNIVERSITY  
OF IOANNINA

# Synthesis and characterization of novel vanillin-based polyesters

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<https://bikiarislaboratory.com>

# Background

- Most commodity plastics are fossil-based

*Issues:* ✘ Progressive depletion of fossil resources

✘ Fluctuating oil price

*Solution*

✔ Biomass valorization for new environment friendly polymers

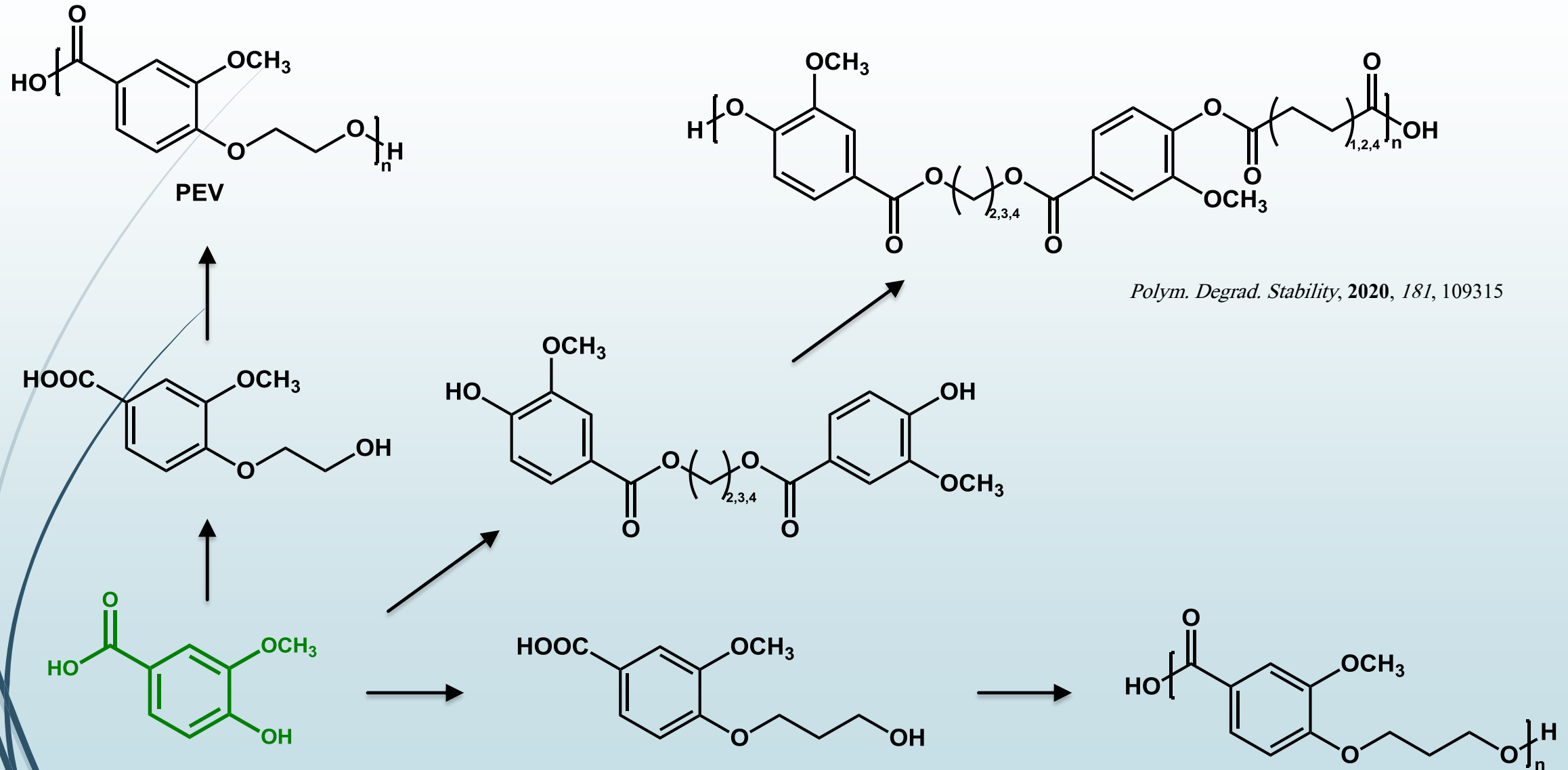
- Lignin

Renewable, non-edible, low-cost by-product of the paper industry

Valorization in the production of novel bio-based monomers

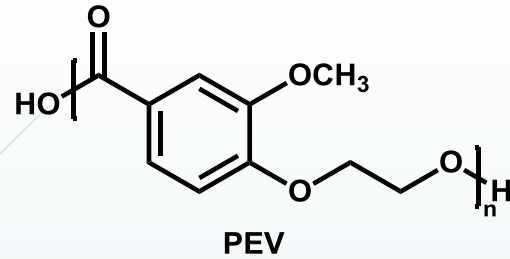
- Vanillin produced from lignin is already commercially available.
- Vanillic acid, an aromatic hydroxy-acid, can be readily produced from vanillin by oxidation.

# Bio-based monomers and corresponding polyesters

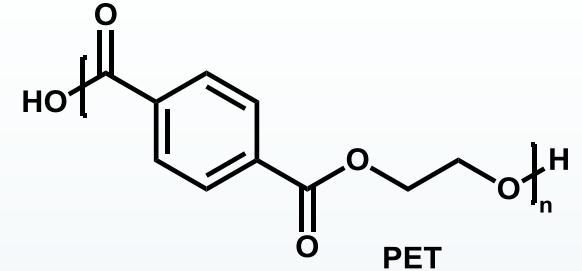


*Towards novel lignin-based aromatic polyesters: Synthesis and thermal behavior of poly(propylene vanillate) by Zoi Terzopoulou et al.!!!!*

# Poly(ethylene vanillate), PEV

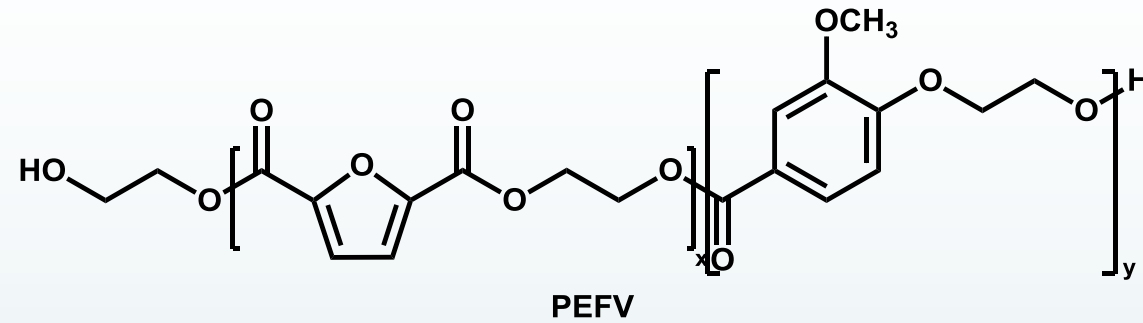


structurally similar to

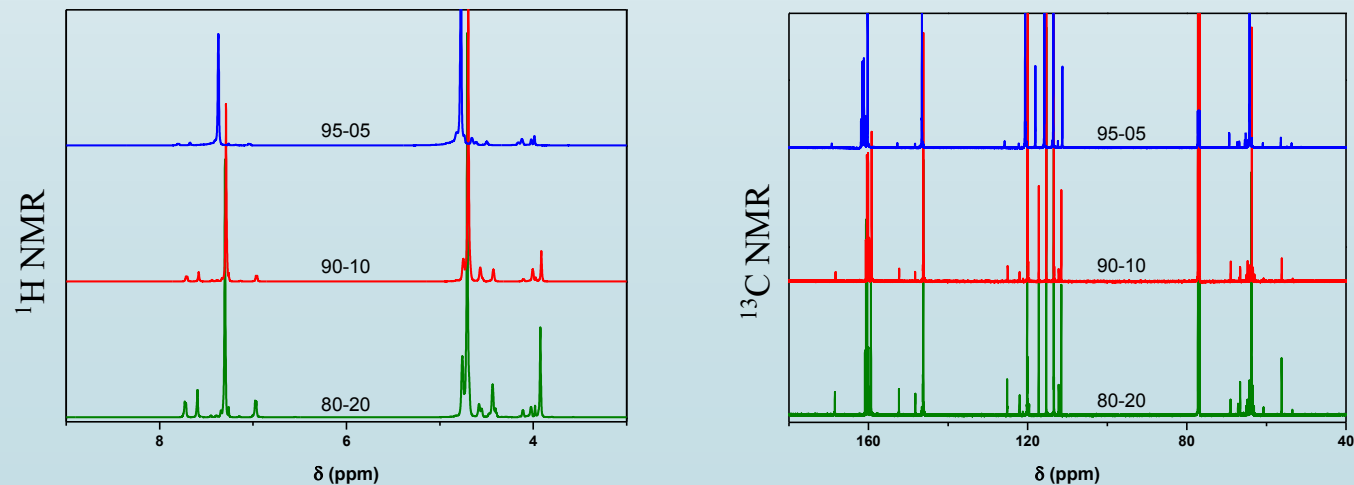


- ▶  $T_g$  83 °C,  $T_m$  261 °C (comparable to PET  $T_g$ =80 °C and  $T_m$ =252 °C).
- ▶  $\Delta H_m^\circ$  166 ± 16 J/g, equilibrium melting temperature ( $T_m^0$ ) 301.4 °C.
- ▶ Slow crystallization attributed to poor nucleation density.
- ▶ Thermal stability: 1% mass loss at 327 °C, maximum decomposition rate at ~420 °C.
- ▶ Thermal degradation mechanism (Py-GC/MS):
  - heterolytic scission characteristic of ester bonds, and
  - extensive C-O and C-C homolytic cleavage attributed to the ether linkage.
- ▶ Mechanical properties (nanoindentation): hardness close to PET.

# Copolymers with ethylene furanoate



- ▶ Successful copolymerization demonstrated by NMR, probably block structure.
- ▶  $T_g$ s around 80 °C.
- ▶ Lower thermal stability compared to poly(ethylene furanoate).



# Conclusions

- ▶ Vanillic acid is an interesting bio-based monomer for the synthesis of sustainable thermoplastics.
- ▶ Poly(ethylene vanillate) is a promising ether-containing polyester, with thermal properties comparable to PET.
- ▶ Poly(propylene vanillate) has exhibited remarkable thermal properties.
- ▶ Copolymers with ethylene furanoate are under investigation.



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