Ca' Foscari University of Venice

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NEW FAMILIES OF 5-HMF DERIVED BIOPOLYMERS VIA ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

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INTRODUCTION

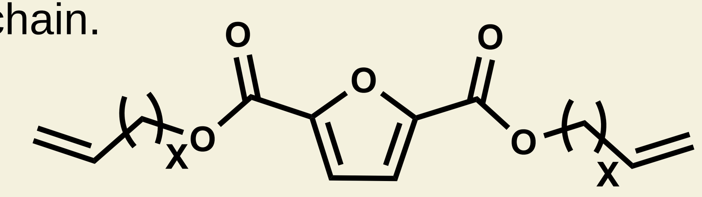
Over the last two decades, there has been a growing demand for renewable feedstock as an alternative to finite resources like petroleum. As a result, all industries, including the plastic industry, are transitioning to more sustainable approaches when developing their products.[1] This has led to a rising interest in using natural resources, such as 5-hydroxymethylfurfural (5-HMF) for the synthesis of renewable monomers that can be used to produce a selection of bio-based polymers.[2] Several 5-HMF derivatives have been discovered as monomers that can improve the thermal and mechanical characteristics of the resulting polymer.[3] With that in mind, in this project we developed new furanic bio monomers, starting from the HMF derivative 2,5-furandicarboxylic acid dialkyl ester (FDME), that can be used has building block to synthetize via acyclic diene metathesis (ADMET) polymerization, several families of furanic based biopolymers.

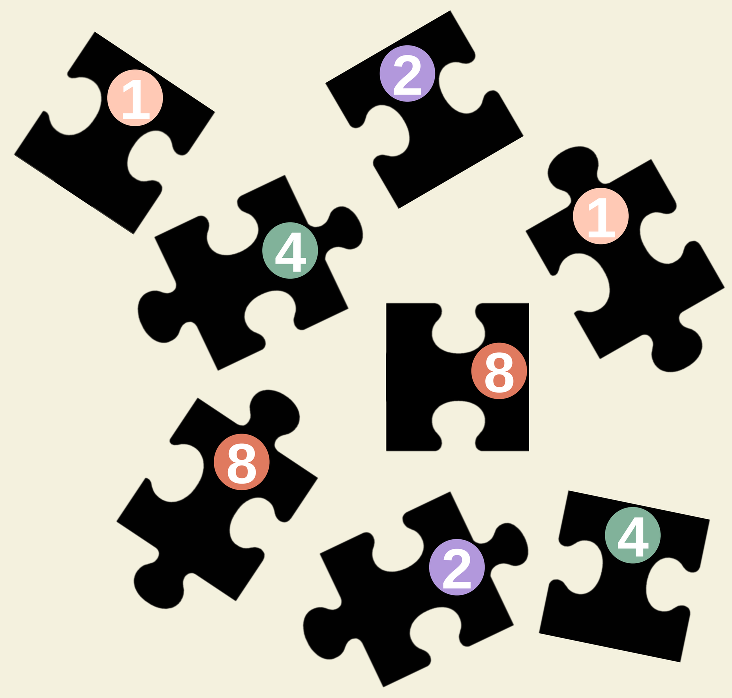
METHODOLOGY

1st Step

Synthesis of furanic α,ω-diene monomers

In this first step FDME based α,ω-diene monomers were synthesized/ optimized by a trivial transesterification reaction producing 4 different α,ω-diene monomers with different lengths alkene chain.



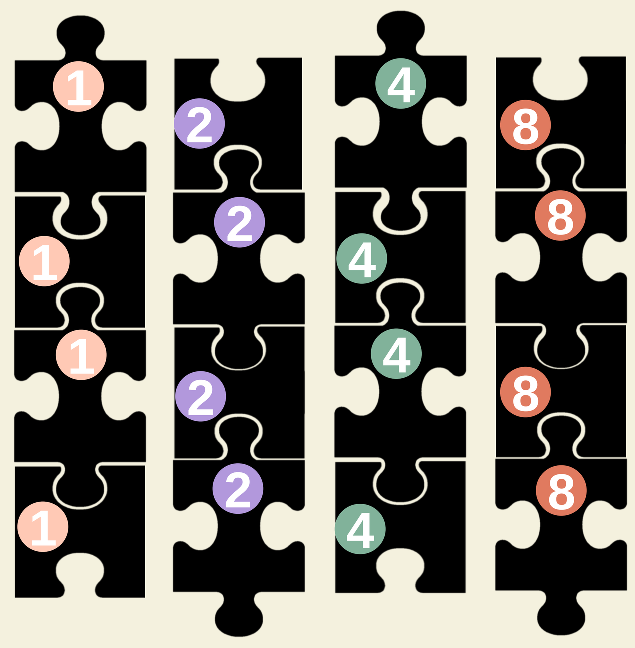


2nd Step

ADMET polymerization

Homopolymers

In the second step each furanic α,ω-diene monomer was polymerized via ADMET polymerization using several different metathesis catalysts, in order to study the effects of the alkene chain length on the rigidity and thermal properties of the synthesized polymer.

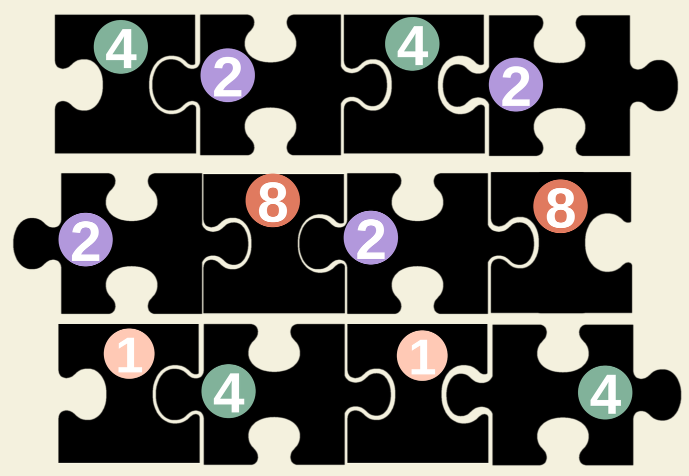


3rd Step

ADMET polymerization

Copolymers

In the third step copolymers were attended using the optimized conditions of the ADMET polymerization of homopolymers, combining the longest members of the α,ω-diene family with the shortest, in order to enquire any changes in behavior of the polymer with the addition of a shorter monomer.

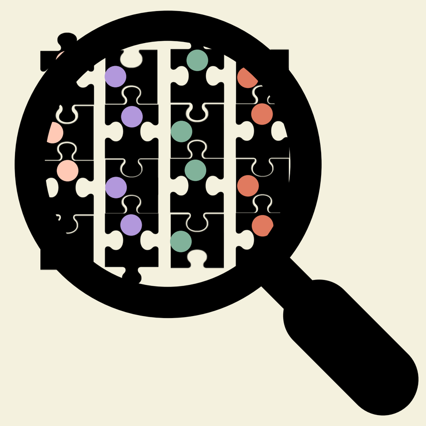


4th Step

Characterization

The polymers synthesized were all fully characterized in order to evaluate their molecular weight, thermal properties and structure.

- NMR Spectroscopy
- Size Exclusion Chromatography (SEC)
- Thermogravimetric Analysis (TGA)
- Differential Scanning Colometry (DSC)



RESULTS AND DISCUSSION

Monomer synthesis

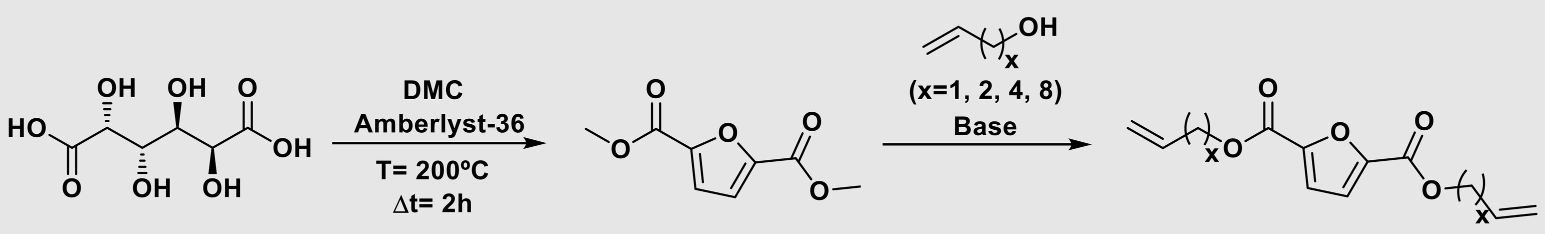


Table 1: Optimized conditions for the synthesis of furanic α,ω-diene monomers

Alcohol used	T(ºC)	t (h)	Conv (%)	Selectivity		NMR yield (%)	Isolated yield (%)
				Asymmetric	Symmetric		
Prop-2-en-1-ol	90	3	100	3	97	68	-
But-3-en-1-ol	100	24	100	-	100	75	75
Hex-5-en-1-ol	120	24	100	-	100	63	63
Dec-9-en-1-ol	120	24	100	3	97	-	41

Polymerization of homopolymers

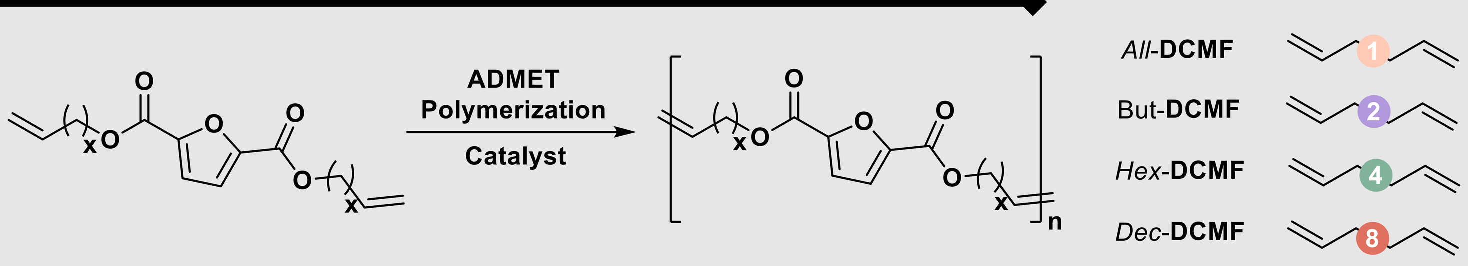
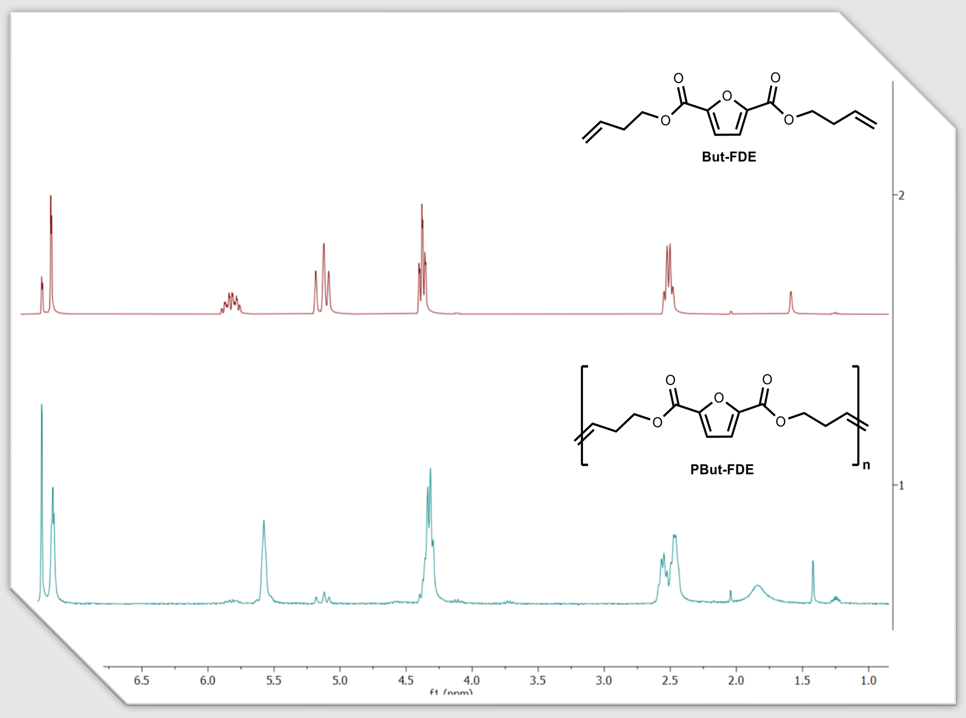
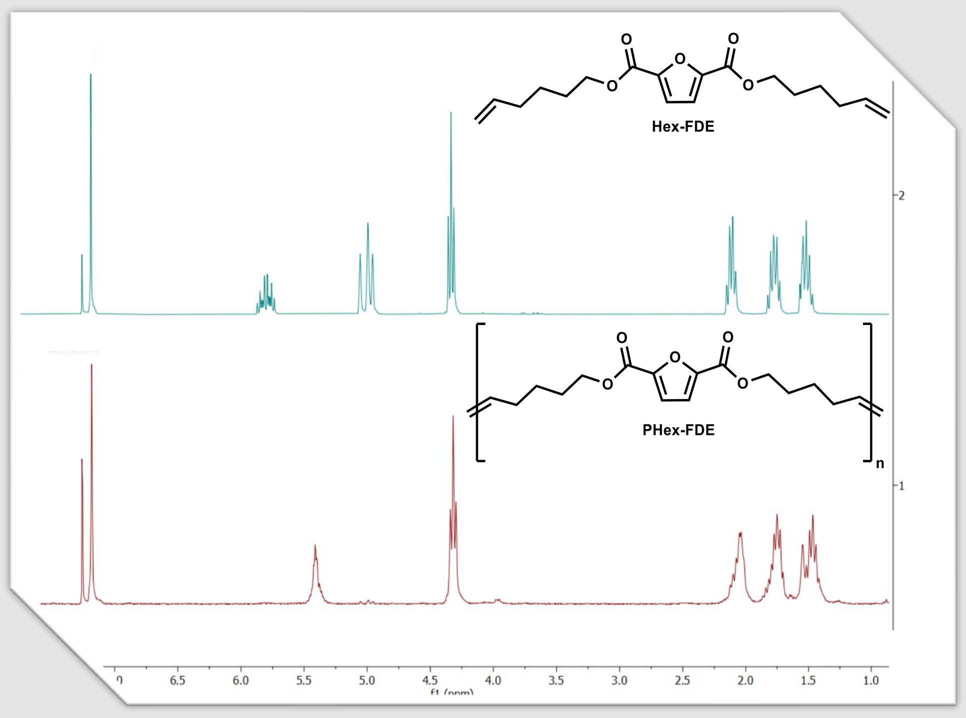
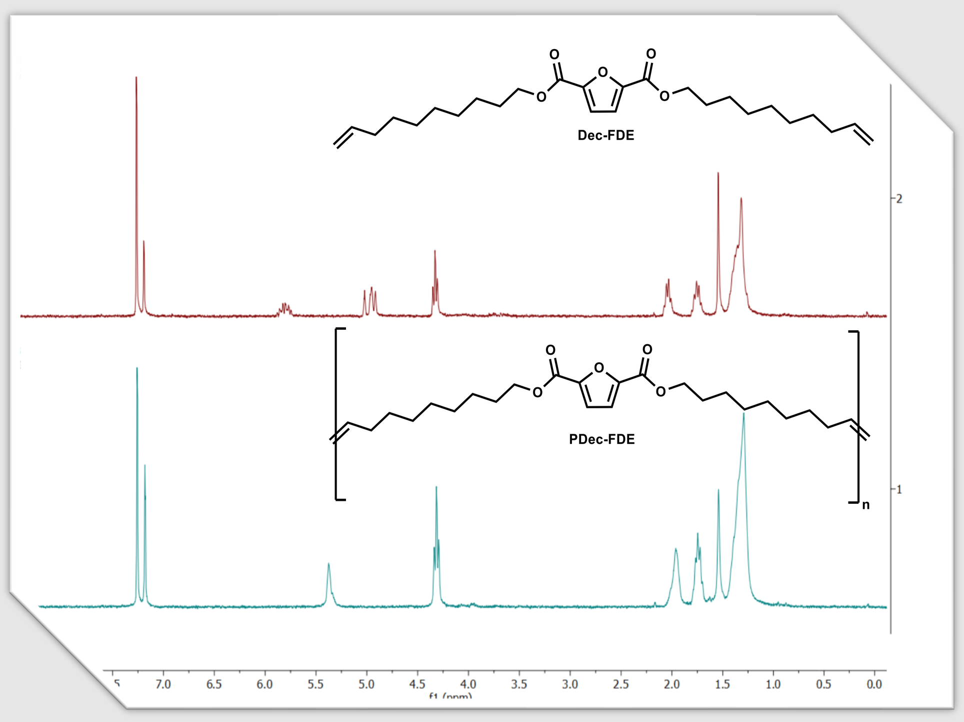


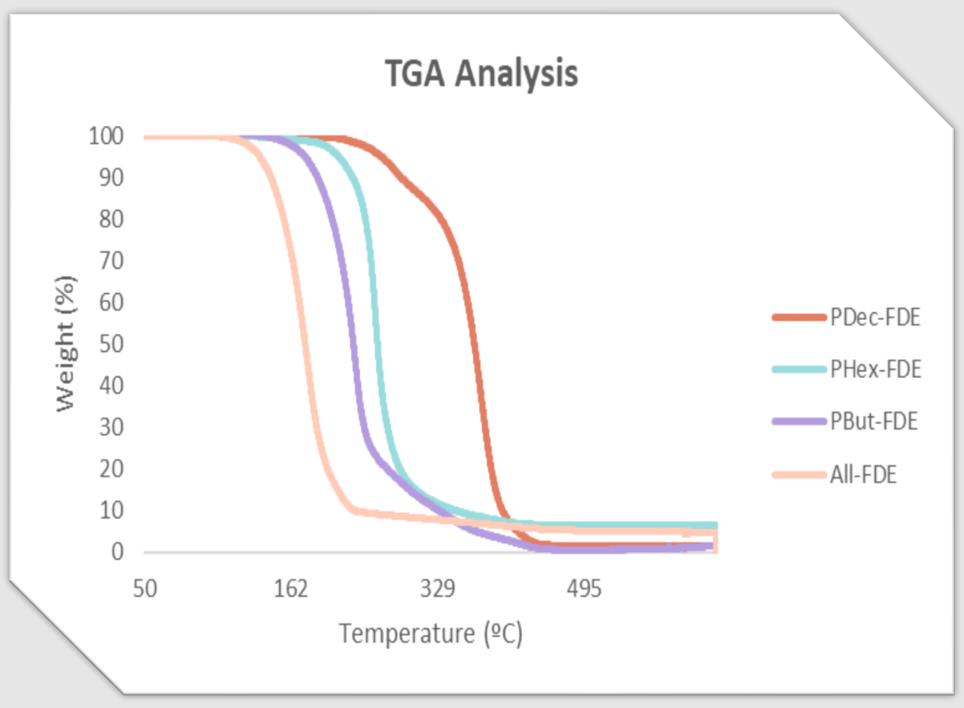
Table 2: ADMET polymerization for the different furanic α,ω-diene monomers

Monomers	t (h)	Conv (%)	Yield (%)	Mn (kDa)	D	$Td_{5\%}$ (ºC)	T_g (ºC)
FDE-All	24	0	-	-	-	-	-
FDE-But	24	85	20	3.2	1.30	192	8
FDE-Hex	1	100	59	12.2	2.13	208	-16
FDE-Dec	0.5	100	57	19.3	2.20	265	-31









CONCLUSIONS

- Development of optimized reaction conditions for the synthesis of 4 different furanic α,ω-diene monomers, in high yield;
- Development of custom-made purification procedure;
- Solvent free ADMET polymerization was performed in bulk using several different metathesis catalyst to synthesize homopolymers;
- It was noted that the longer the alkene chain of the monomer was the heavier the polymer as well as better thermic properties;
- For future work ADMET polymerization will be conducted in solvent as well as copolymers will be attempted.

[1] Zhang, D. & Dumont, M. J. Advances in polymer precursors and bio-based polymers synthesized from 5-hydroxymethylfurfural. *Journal of Polymer Science, Part A: Polymer Chemistry* vol. 55 1478–1492 (2017); [2] Xu, C., Paone, E., Rodríguez-Padrón, D., Luque, R. & Mauriello, F. Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural. *Chemical Society Reviews* vol. 49 4273–4306 (2020); [3] Jiang, M., Liu, Q., Zhang, Q., Ye, C. & Zhou, G. A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources. *J Polym Sci A Polym Chem* **50**, 1026–1036 (2012).