New families of 5-hydroxymethylfurfural derived biopolymers

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INTRODUCTION

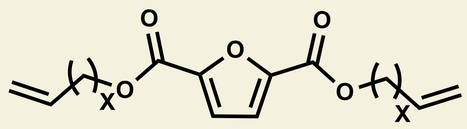
Over the last two decades, there has been a growing demand for renewable feedstock as an alternative to finite resources like petroleum. As a result, all industries, including the plastic industry, are transitioning to more sustainable approaches when developing their products.[1] This has led to a rising 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

Firstly, FDME based α,ω-diene monomers were synthesized producing 4 different α,ω-diene monomers with different lengths alkene chain.



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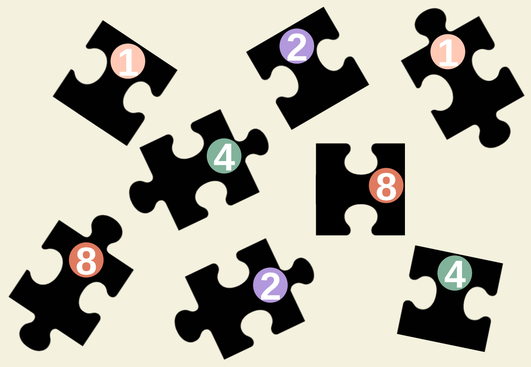


2nd Step

ADMET polymerization

Homopolymers

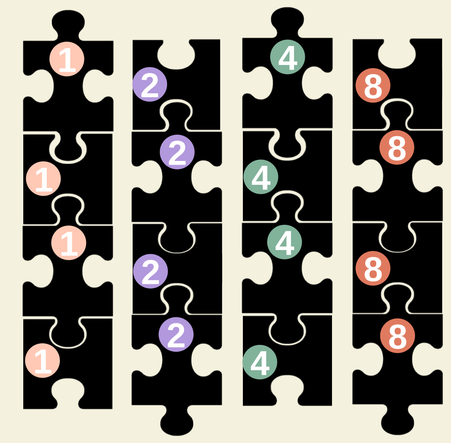
In the second step each furanic α,ω-diene monomer was polymerized via ADMET polymerization using several different metathesis catalysts, in order to study the effects of the alkene chain length on the rigidity and thermal properties of the synthesized polymer. Trials were done both in neat and with solvent.

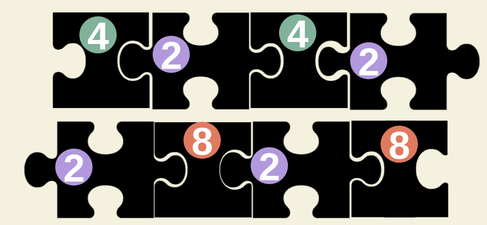
3rd Step

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

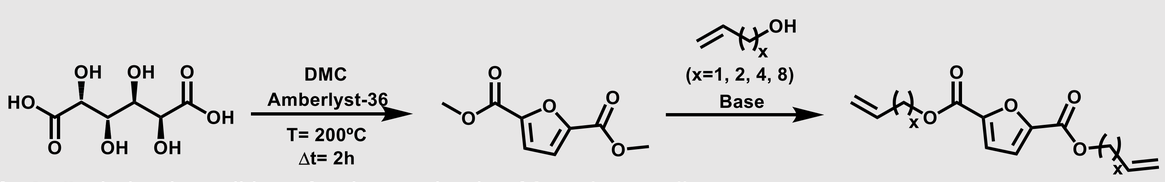


Table 1: Optimized conditions for the synthesis of furanic α,ω-diene monomers.

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

Polymerization of Homopolymers

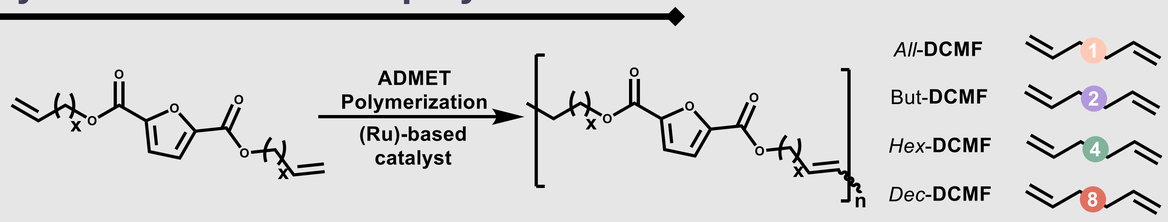
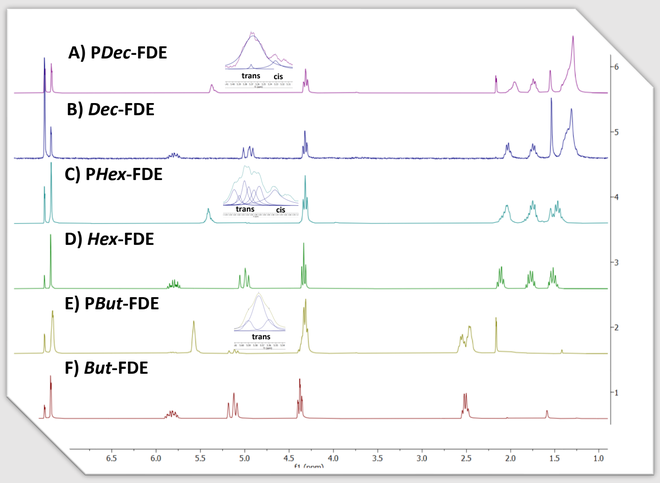


Table 2: ADMET polymerization for the different furanic α,ω-diene monomers[a]

Monomers	t (h)	Conv. (%)[b]	Yield (%)[c]	Mn (kDa)[d]	*Đ*[e]	$T_{d5\%}$ (ºC)[f]	T_g (ºC)[g]
All-FDE	24	0	-	-	-	-	-
But-FDE	24	85	20	3.2	1.30	192	8
Hex-FDE	1	100	59	12.2	2.13	208	-16
Dec-FDE	0.5	100	57	19.3	2.20	265	-31

[a] Duration required to attain full conversion as determined by ^{1}H NMR, with maximum time of 24 h; [b] Conversion was calculated trough NMR; [c] Isolated yield after purification and drying, yield = (isolated mass/theoretical mass) × 100; [d] Determined by SEC in THF (10 mM LiBr) at 50 °C; [e] *Đ* = dispersity. [f] TGA degradation temperatures at which 5% ($T_{d5\%}$) mass loss was observed under nitrogen; [g] Glass transition temperature determined by DSC, temperature ramp 10 °C min^{-1};



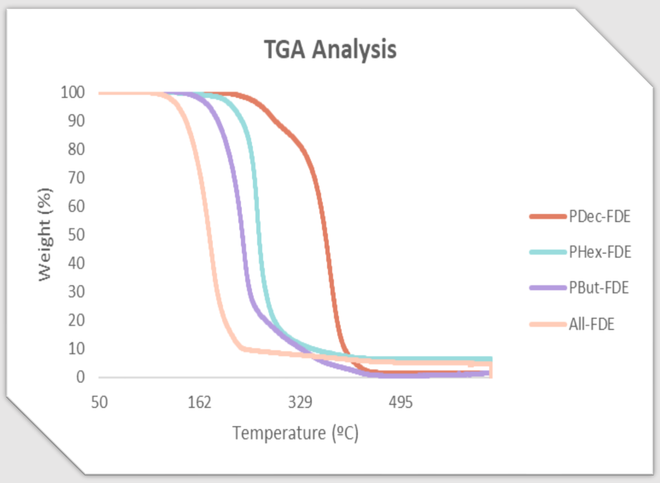
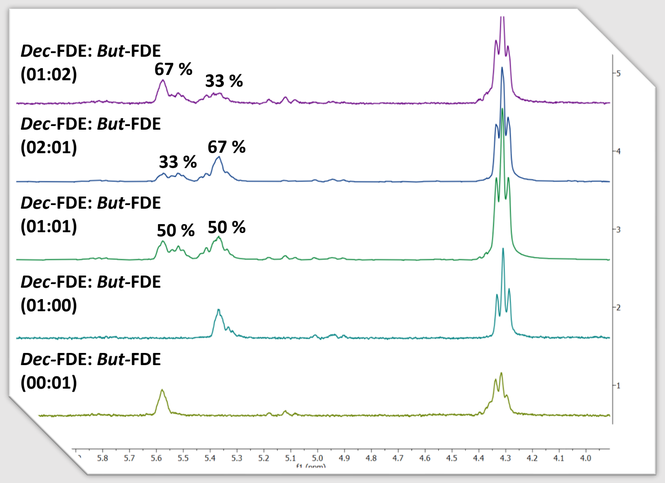


Figure 1. ^{1}H NMR spectroscopy of the polymer and their respective monomer (Left); Comparison of TGA analysis for the homopolymers synthetized (Right).

Polymerization of Copolymers

Co-polymerization trials were conducted mixing different amounts of *Hex*-FDE or *Dec*-FDE with *But*-FDE. Data collected showed that both monomers were incorporated into the copolymer while maintaining their related ratio in the final product.



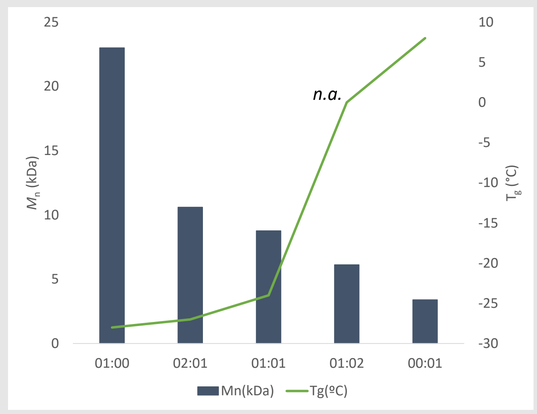


Figure 2. ^{1}H NMR spectra *Dec*-FDE copolymer with *But*-FDE with respective monomer ratios calculated trough NMR; Graphical comparison of M_n and T_g between the different synthesized co-polymers; *n.a.* = value not available.

CONCLUSIONS

- Development of optimized reaction conditions for the synthesis of 4 different furanic α,ω-diene monomers, in high yield;
- 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;
- ADMET polymerization employing green solvents (such as Cyrene™, dimethyl isosorbide (DMI), and γ-valerolactone (GVL)) was conducted, demonstrating less efficiency than neat polymerization.
- Co-polymerisation attempts between mixing different amounts of *Hex*-FDE or *Dec*-FDE with *But*-FDE were successful.

[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).