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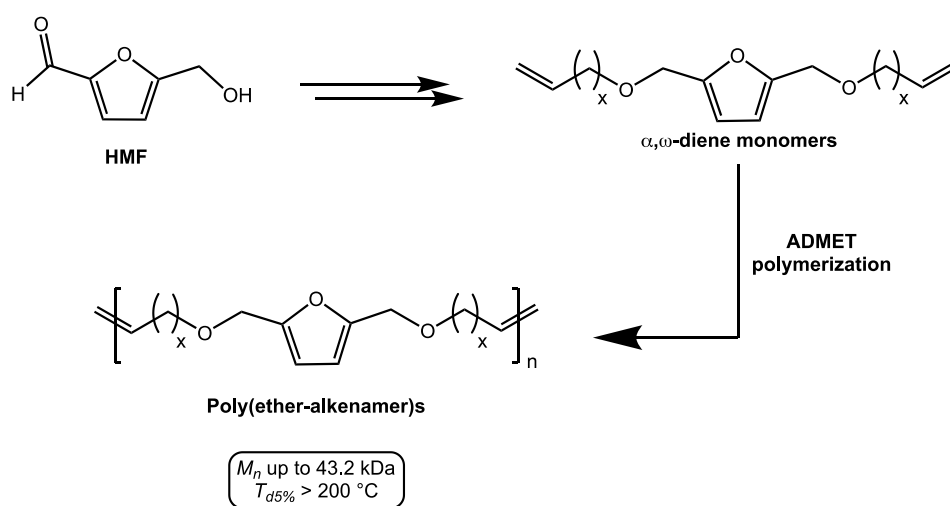
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Bio-based Polyethers via ADMET Polymerization of α,ω -Diene Furanics

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KEYWORDS. ADMET polymerization, 2,5-bis(hydroxymethyl)furan (BHMF), Bio-based α,ω -Dienes, Green solvents, Cyrene™.

ABSTRACT: A new class of furanic α,ω -dienes was synthesized using cellulose-derived 2,5-bis(hydroxymethyl)furan (**BHMF**) as a renewable starting material. The ability of these monomers to undergo acyclic diene metathesis (ADMET) polymerization was investigated under various reaction conditions, including type of metathesis catalyst and catalyst loading. The resulting bio-based polyethers were characterized through high-performance size exclusion chromatography (HPSEC), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The novel polymers showed molecular weights up to 43 kDa and exhibited good thermal stability ($T_{d5\%} > 250$ °C) and low glass transition temperatures (-67 °C $< T_g < -24$ °C). Polymerization reactions were also conducted employing selected green solvents (Cyrene™, dimethyl isosorbide and γ -valerolactone) and the results were compared to the solvent-free procedure. Finally, in order to increase the T_g values of the polyethers, co-polymerization experiments were performed employing the best performing furanic α,ω -diene as well as a bio-based aromatic monomer derived from syringaresinol.

1. Introduction

Pollution generated by the production, use and discard of plastics is a rising concern. One part of the solution involves harnessing biomass as a means to reduce greenhouse emissions.

Bio-based building blocks have been investigated as potential substitutes for petroleum-based monomers. Among them, hydroxymethyl furfural (HMF) can be achieved in high yield *via* the dehydration of carbohydrates (mainly D-fructose),^{1,2} the acid-catalyzed hydrolysis/dehydration of cellulose,³ and more recently also starting from food waste.⁴⁻⁷ This bifunctional aromatic platform molecule can be further derived into promising compounds (Figure 1), including 2,5-furandicarboxylic acid (**FDCA**),^{8,9} 2,5-bis(hydroxymethyl)furan (**BHMF**),^{10,11} 2,5-bis[(oxiran-2-ylmethoxy)methyl]furan,^{12,13} 2,5-bis(aminomethyl)furan (**BAF**),¹⁴ 2,5-

polymer architectures.³¹ The ease of handling metathesis catalysts, particularly those based on ruthenium, along with their remarkable tolerance toward a diverse range of functional groups, has allowed the exploration of various substrates including fatty acids,^{31–33} castor oil derivative,^{34,35} ferulic acid derivatives,³⁶ sinapic acid derivative,³⁷ and some sugar-based monomers such as isosorbide α,ω -dienes.³⁸ Preliminary investigation was carried out on a specific α,ω -diene monomer derived from **BHMF**, namely 2,5-bis(hydroxymethyl)furan undecenoate (**BHMFU**, Figure 1). However, only a single in-solvent ADMET condition was examined, resulting in the production of homopolyester of **BHMFU** with a reported molecular weight (M_n) of 10 kDa. This monomer was also used for the synthesis of copolymers with isosorbide and glucarodilactone derived monomers.³⁹

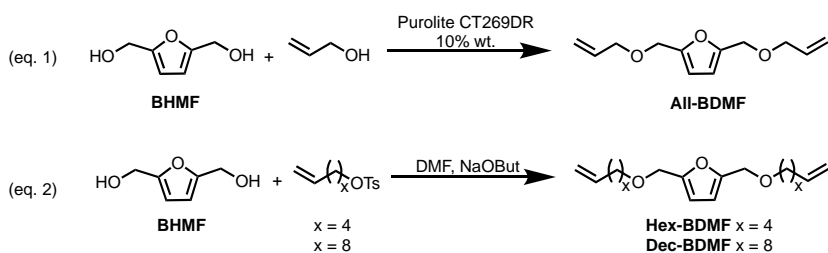
In this work, we focus on the synthesis of a novel class of furan-based α,ω -dienes (**BDMFs**) using **BHMF** as a renewable starting material. These monomers, incorporating olefins with different chain length, were then investigated for their ability to undergo ADMET polymerization under different conditions, allowing for precise control over the thermal properties of the resulting polymers. We also explored the use of green media in polymerization reactions and performed co-polymerization experiments to enhance the properties of the resulting bio-based furanic polyethers.

2. Results and Discussion

2.1. Monomers preparation

BHMF employed for the synthesis of the α,ω -diene monomers was prepared in multigram scale according to our recently published procedure.⁴⁰ Initially, we aimed to employ a straightforward acid-catalyzed etherification reaction for the production of the **BHMF**-based

monomers. Thus, Purolite CT269DR, a macroporous catalyst characterized by sulfonic groups, was selected as the acidic heterogenous catalyst since it was demonstrated efficient in the synthesis of a library of **BHMF**-derived alkoxy monomers including 2,5-bis((allyloxy)methyl)furan (*All-BDMF*) already available in our laboratories in gram scale (eq. 1; Scheme 1).⁴¹ However, when this procedure was attempted for the etherification of **BHMF** with hex-5-enol and dec-9-enol, the related α,ω -diene monomers *Hex-BDMF* and *Dec-BDMF* formed only in scarce amounts, probably due to the lower reactivity of these alcohols under acidic conditions. These α,ω -diene monomers were then synthesized according to a two-step procedure, i.e., tosylation of the starting enols followed by a base-catalyzed nucleophilic substitution with **BHMF** (eq. 2; Scheme 1). The chemical structures of *Hex-* and *Dec-BDMF* were confirmed by NMR spectroscopy and High-Resolution Mass-Spectrometry (Hi-Res MS) analysis. Furthermore, all three α,ω -diene monomers were purified via column chromatography so to ensure high purity samples for the ADMET polymerization.



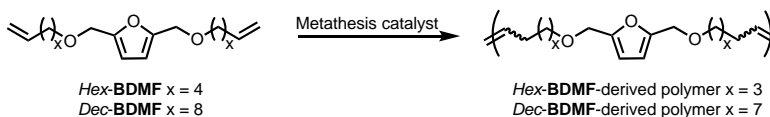
Scheme 1. Synthesis of the α,ω -diene BHMF-derived monomers.

2.2. ADMET Polymerization

2.2.1. Solvent-free ADMET polymerization of the α,ω -diene **BHMF**-derived monomers

The impact of the monomer chain length on ADMET polymerization has been well documented in previous research works.^{36,37,42} As expected, the current study revealed that the

use of *All*-**BDMF** only resulted in the formation of oligomers ($M_w = 1.4$ kDa). On the other hand, *Hex*-**BDMF** and *Dec*-**BDMF** demonstrated more promising outcomes when polymerized in the presence of Hoveyda-Grubbs second generation catalyst (HGII) (Scheme 2; Table 1). Based on these findings, *Dec*-**BDMF** was selected for further screening experiments (#1-11; Table 1).



Scheme 2. ADMET polymerization of **BDMF**-derived monomers

Six ruthenium-based catalysts were investigated in addition to HGII (Figure 2), specifically, 1st and 2nd generation of Grubbs catalysts (GI and GII), a derivative of GII with mono-*ortho*-substituted *N*-heterocyclic carbene (NHC) (M205), a Grubbs type catalyst incorporating a sulfonamide moiety (Zhan catalyst-1B), one incorporating a ketone moiety (M510) and 3rd generation of Grubbs catalysts (M300) (Figure 2; #1-7, Table 1).

Classical ADMET polymerization conditions were used for this screening.^{30,36} The experiments were carried out in bulk at a temperature of 80 °C under reduced pressure (25 mbar) in the presence of 1.0 mol% of catalyst and 2.0 mol% of *p*-benzoquinone to avoid isomerization.⁴³ Vacuum was applied to ensure complete removal of the ethylene produced during the reaction and to favor polymerization.

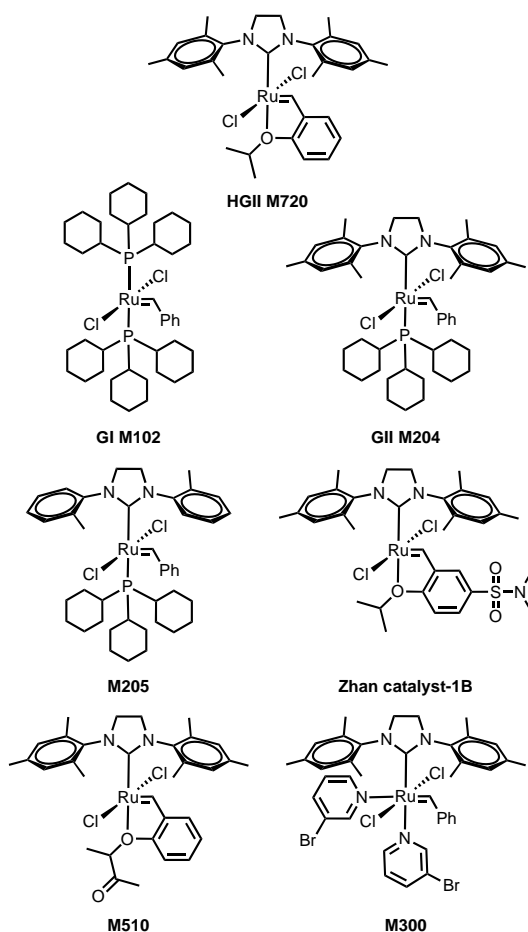


Figure 2. Structure of the seven ruthenium-based catalysts tested.

The conversion of *Dec-BDMF* was monitored by ^1H NMR. The disappearance of the alkene proton signals at 4.96 and 5.80 ppm was used to calculate the monomer conversion, while the appearance of a signal at 5.36 ppm indicated the formation of polymers. Total conversion of the starting monomer was observed for five of the seven tested catalysts after only 2 h, i.e., HGII, GI, GII, Zhan catalyst and M510. High conversion (94%) was recorded for M300 after 2 h, while the polymerization catalyzed by M205 led only to 72% of conversion. This latter experiment was stopped after 4 h since no further increase in the conversion of *Dec-BDMF* was observed. In all trials, no evidence of isomerization or ring-closing metathesis (RCM) was detected, even in the presence of M205, a well-known catalyst for RCM.⁴⁴ These results provide further confirmation

of previously reported data, supporting that long chain terminal olefins (i.e., hexene, decene), undergo preferentially polymerization over RCM.³⁶

The recovered polymers showed different aspects from light brown sticky oil to dark grey agglomerate and this diversity was related to their thermal properties (*vide infra*).

Furthermore, the so-prepared polyethers were analyzed using HPSEC, revealing significantly higher molecular weights for polymers produced using GI ($M_w = 36.4$ kDa), GII ($M_w = 28.1$ kDa) and Zhan ($M_w = 25.8$ kDa) catalyst. Surprisingly, GI displayed the highest activity, despite its known vulnerability to high temperatures.⁴⁵ It is worth noting that the specified temperature of 80 °C represents the heating bath rather than the actual flask temperature. Moreover, the application of vacuum (25 mbar), initially intended for ethylene removal, potentially prevented the degradation of the catalyst by reducing the temperature inside the flask.

According to the data collected on the ADMET polymerization of *Dec-BDMF*, GI was selected as the best performing catalyst. Further optimization experiments were conducted using GI to investigate the effect of the temperature (#8-9; Table 1) and catalyst loading (#10-11; Table 1) on the ADMET polymerization. Additionally, it is worth mentioning that GI is also the most cost-effective option among the catalysts investigated in this study.

Table 1. ADMET polymerization using *Dec-BDMF* or *Hex-BDMF* as substrates.

#	Monomer	Catalyst	Cat. amount (mol%)	Temp. (°C)	Time (h)	Conv. (%)	M_n (kDa)	M_w (kDa)	\bar{D}	T_g (°C)	$T_{d5\%}$ (°C)	T_m (°C)	T_c (°C)
1	<i>Dec-BDMF</i>	HGII M720	1.0	80	2	100	9.5	16.8	1.8	-53.3	257	21	4.2
2	<i>Dec-BDMF</i>	GI M102	1.0	80	2	100	19.1	36.4	1.9	-52.3	275	56	8.4
3	<i>Dec-BDMF</i>	GII M204	1.0	80	2	100	15.3	28.1	1.8	-62.1	270	21	-3.6
4	<i>Dec-BDMF</i>	M510	1.0	80	2	100	9.7	17.7	1.8	-54.5	258	23	-2.5
5	<i>Dec-BDMF</i>	M205	1.0	80	2	72	4.8	8.2	1.7	-55.2	277	56	12.6
6	<i>Dec-BDMF</i>	Zhan Cat.-1B	1.0	80	2	100	14.3	25.8	1.8	-52.0	265	49	-3.7
7	<i>Dec-BDMF</i>	M300	1.0	80	2	94	3.9	6.5	1.7	-54.3	244	44	-2.5
8	<i>Dec-BDMF</i>	GI M102	1.0	60	2	88	21.3	43.2	2	-50.1	293	57	8.7
9	<i>Dec-BDMF</i>	GI M102	1.0	100	2	100	13.8	25.3	1.8	-24.0	275	50	4.9
10	<i>Dec-BDMF</i>	GI M102	5.0	80	2	100	16.7	33.4	2	-49.1	281	56	12.2
11	<i>Dec-BDMF</i>	GI M102	0.5	80	4	94	14.9	30.7	2.1	-50.8	301	55	9.7
12	<i>Hex-BDMF</i>	GI M102	1.0	80	2	100	12.2	25.4	2.1	-64.0	263	-	-
13	<i>Hex-BDMF</i>	HGII M720	1.0	80	2	100	6.0	9.8	1.6	-66.9	207	-	-
14	<i>Hex-BDMF</i>	Zhan Cat.	1.0	80	2	100	10.1	19.1	1.9	-63.6	230	-	-
15	<i>Hex-BDMF</i>	GI M102	5.0	80	2	100	18.5	37.6	2	-60.1	231	-	-
16	<i>Hex-BDMF</i>	GI M102	0.5	80	24	100	13.0	26.0	2.0	-45.1	240	-	-

Increasing the reaction temperature resulted in a decreased reaction time; full conversion of *Dec-BDMF* was observed after 2 hours at 80 and 100 °C compared to 88% at 60 °C (#2, #8-9; Table 1). However, higher temperature was accompanied by a reduction in the molecular weight of the bio-based polymer as shown in Figure 3. This phenomenon can be ascribed to the lower thermal stability of the GI catalyst. Consequently, 80 °C was selected as the optimal temperature that balances both rapid reaction kinetics and improved polymerization.

The influence of catalyst loading was not significant, as comparable M_n and M_w values were recorded when 5.0 mol%, 1.0 mol% and 0.5 mol% of GI were employed (#2, #10 and 11, Table 1). It is noteworthy that when the catalyst loading was reduced to 0.5 mol%, the polymerization process required a longer reaction time (#11, Table 1). This can be explained by the fact that a lower catalyst concentration leads to a slower interaction between the catalyst and the substrate, thus delaying the polymerization process. Although the molecular weight of the polymer remained relatively unchanged, the reaction kinetics were affected by the reduced catalyst loading.

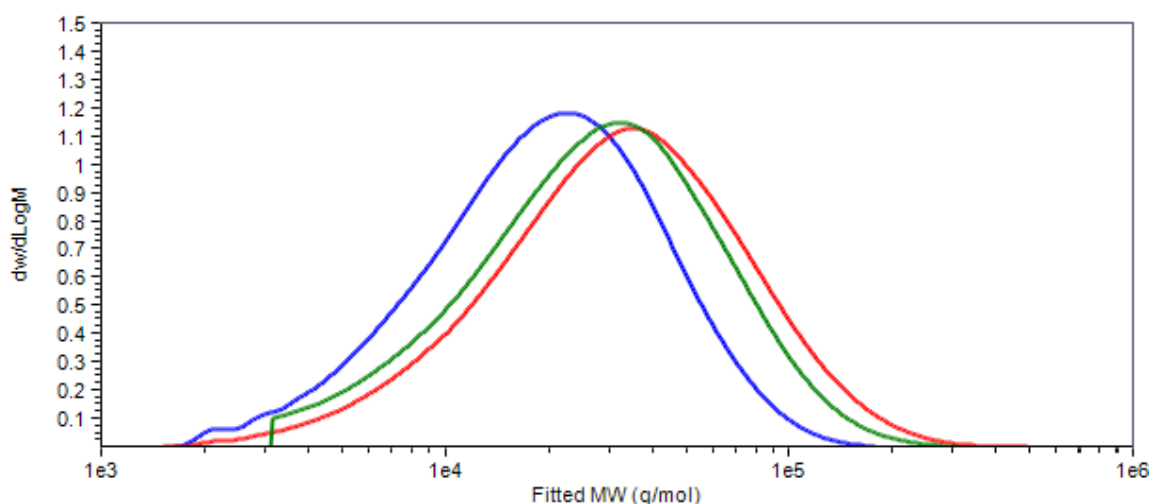


Figure 3. Mass distributions in function of the temperature of polymerization using *Dec-BDMF*, GI 1.0 mol%, solvent-free, 25 mbar at (red) 60 °C (Table 1, #8), (green) 80 °C (Table 1, #2) and (blue) 100 °C (Table 1, #9).

The findings from the *Dec-BDMF* study were subsequently applied to design the ADMET polymerization experiments using *Hex-BDMF* as substrate (#12-16, Table 1). Based on the results achieved, GI and Zhan catalyst were selected as the best performing catalysts. HGII was also tested to assess its reactivity toward the α,ω -diene **BHMF**-derived monomers. Indeed, HGII is often cited as a preferred catalyst for ADMET polymerization.⁴⁶ In the *Hex-BDMF* polymerization, GI displayed high efficiency ($M_w = 25.4$ kDa) followed by Zhan catalyst ($M_w = 19.1$ kDa). HGII also exhibited good activity, achieving complete conversion of the substrate within 2 h, but yielded shorter polymer chains ($M_w = 9.1$ kDa) consistent with the trend observed for *Dec-BDMF* polymerization. Subsequently, the influence of catalyst loading of GI was then investigated. It was observed that similar molecular weights were attained with reduced catalyst loading, however, the polymerization process required an extended time, i.e., 24 h (#15 and 16, Table 1).

2.2.2. ADMET polymerization employing green solvents

Solvent-free polymerization is an appealing choice in terms of green chemistry perspective, as it eliminates the necessity for potentially toxic or environmentally harmful solvents. However, practical implementation of solvent-free polymerizations can lead to highly viscous reaction media, posing challenges in handling and processing of the polymers. To address this issue, some experiments were conducted using green solvents, i.e., CyreneTM, dimethyl isosorbide (DMI) and γ -valerolactone (GVL). The solvents were selected instead of classical organic

solvents to ensure the sustainability of the polymerization. Previous investigations were reported on ADMET polymerization using several green solvents, with Rhodiasolv® Polarclean - whose main component is methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate. With its high boiling point, Polarclean allows reaction conditions similar to those in bulk.^{33,47} However, this solvent has a proven low compatibility with GI catalyst.⁴⁷ In another example, ADMET polymerization of a sinapic acid derivative was explored employing Cyrene™ as solvent, but in the presence of HGII catalyst.³⁷ Herein, we investigated the use of Cyrene™, dimethyl isosorbide (DMI) and γ -valerolactone (GVL) (Figure 4), for ADMET polymerization employing GI catalyst. These solvents were chosen due to their high boiling point ranging from 205 °C (GVL) to 236 °C (DMI), which worked under conditions similar to bulk polymerization, i.e., 80 °C under reduced pressure.

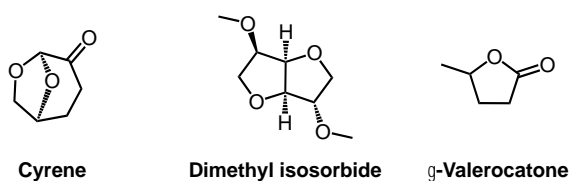


Figure 4. Chemical structures of the green solvents used for ADMET polymerization

Data collected from Table 2 show that conducting ADMET polymerization at high monomer concentration (2.0 and 4.0 mol/L) in Cyrene™ resulted in polymers with high molecular weight as reported in Figure 5. In particular, a three-fold increase in molecular weight ($M_w = 23.4$ kDa) was recorded when the concentration was increased from 2 mol/L to 4 mol/L, under reduced pressure, i.e., 25 mbar (#1 and 2; Table 2). Increasing the pressure from 25 to 50 mbar caused a decrease in molecular weight, with a reduction of over two-fold. Similar molecular weight values

were obtained for ADMET polymerization of *Dec-BDMF* using the three selected solvents at 50 mbar (#3-5; Table 2).

In any case, Cyrene™ emerged as the most effective medium for the polymerization of both *Dec-BDMF* and *Hex-BDMF*. Interestingly, DMI exhibited superior performance as a solvent compared to GVL in the ADMET polymerization of *Hex-BDMF* (#7-8; Table 2).

Table 2. Summary of ADMET polymerization results of *Dec-BDMF* and *Hex-BDMF* employing green solvents.^a

#	Monomer	Solvent	Conc. (mol/L)	Vacuum (mbar)	Yield (%)	M_n (kDa)	M_w (kDa)	\mathcal{D}	T_g (°C)	$T_{d5\%}$ (°C)
1	<i>Dec-BDMF</i>	Cyrene™	2.0	25	n.d	4.6	7.5	1.6	-59	257
2	<i>Dec-BDMF</i>	Cyrene™	4.0	25	n.d	12.1	23.4	1.9	-56	292
3	<i>Dec-BDMF</i>	Cyrene™	4.0	50	87	5.0	9.4	1.9	-55	286
4	<i>Dec-BDMF</i>	DMI	4.0	50	73	5.0	8.7	1.7	-55	291
5	<i>Dec-BDMF</i>	GVL	4.0	50	70	5.5	9.0	1.6	-56	284
6	<i>Hex-BDMF</i>	Cyrene™	4.0	25	n.d	8.2	14.7	1.8	-54	226
7	<i>Hex-BDMF</i>	DMI	4.0	50	66	6.8	12.9	1.9	-62	249
8	<i>Hex-BDMF</i>	GVL	4.0	50	54	4.8	8.2	1.7	-65	263

^a Reactions were conducted at 80 °C for 16 hours using 1.0 mol% GI as catalyst.

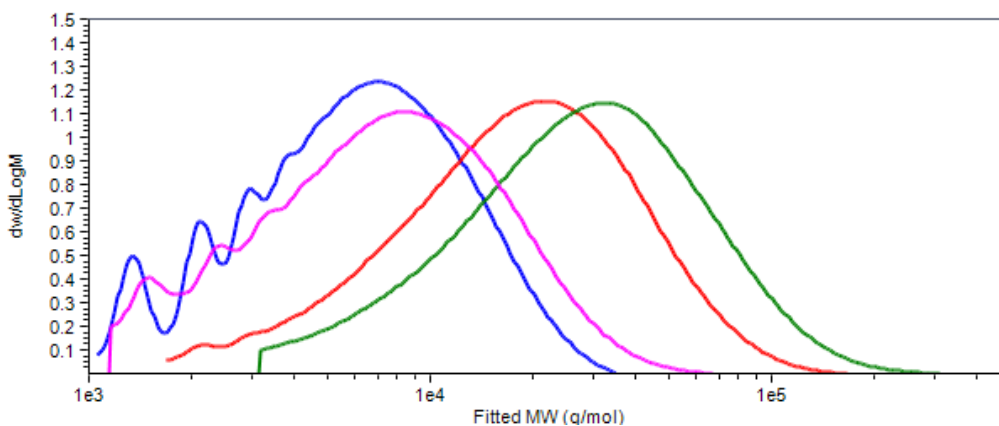


Figure 5. Mass distributions as a function of operating conditions using *Dec-BDMF*, GI 1.0 mol% (green) solvent-free and 25 mbar, (blue) in Cyrene™ at 2.0 mol/L and 25 mbar, (red) in Cyrene™ at 4.0 mol/L and 25 mbar and (pink) in Cyrene™ at 4.0 mol/L and 50 mbar.

2.2.3. Thermal characterization of the novel furanic polyethers

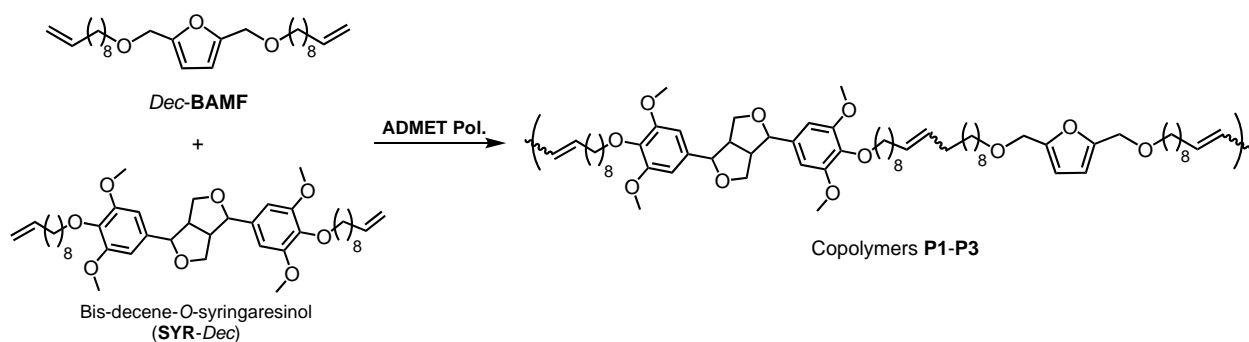
The **BDMF**-derived polymers demonstrated excellent thermal stability, as evidenced by degradation temperatures ($T_{d5\%}$) exceeding 200 °C and specifically within the 250-290 °C range (Table 1-2). The polymer obtained from *Dec-BDMF* exhibited melting and crystallization transitions (Figures S2). Polymer oils displaying a highly sticky behaviour exhibited melting transitions at approximately 20 °C and were obtained using GII, HGII and M204. Conversely, polymers synthesized with GI, M205, and Zhan catalysts exhibited agglomerates due to their melting transitions occurring above 45 °C. The polymer obtained through ADMET polymerization with M300 displayed a T_m of 44 °C and presented a distinctive appearance of agglomerates embedded within a sticky matrix. However, in the DSC analysis of the polyethers obtained from *Hex-BDMF*, none of these transitions were observed (Figure S7). One can hypothesize that furan moieties disrupted the arrangement of the linear chains. Such disruption was recorded for poly(ethylene-*co*-acrylic acid) polymers where no melting point was observed due to the pendant acidic moieties.⁴⁸ In the *Hex-BDMF* derived polymers the frequency of the furan moieties would prevent the formation of a crystal structure whereas longer linear chains in *Dec-BDMF*-derived polymers would allow this arrangement.

Due to the high flexibility of the monomers used, the resulting bio-based polymers displayed very low T_g s, with values below -50 °C, as reported in Table 1-2. Interestingly, when comparing the monomers of *Hex-BDMF* and *Dec-BDMF*, it can be observed that the use of *Hex-BDMF* led to even lower T_g values. This finding contradicts to the results obtained in the ADMET

polymerization of macrobisphenols and syringaresinol derivatives,^{36,49} Indeed, longer chain length was anticipated to increase flexibility and hence result in lower T_g values. However, it is possible that *Hex-BDMF* possesses certain molecular attributes that result in a less constrained polymer structure, leading to higher T_g values compared to *Dec-BDMF*. Similarly, in a study reported by Moser *et al.* on renewable aliphatic polyesters from fatty dienes, it was also observed an increase in T_g values with increasing chain length of the monomer.⁵⁰ Future investigation via molecular modeling study could help to analyze the specific molecular interactions and structural factors influencing the T_g values of the polymers derived from *Dec-BDMF* and *Hex-BDMF*. It is also important to note that, for polymers derived from *Dec-BDMF*, T_g transitions were broad on the DSC chromatograms, leading to a certain approximation with difficulties to pinpoint the exact values (Figure S1). Furthermore, as the T_g is extremely low, the DSC apparatus was pushed to its limits, despite using a very modest temperature gradient of 2 °C/min.

2.2.4. Copolymerization with **SYR-*Dec***

A well-known strategy to increase T_g values of a polymer is to incorporate into its backbone a more rigid monomer containing aromatic moieties.⁵⁰ With this in mind, *Dec-BDMF* was copolymerized with the previously reported α,ω -diene of syringaresinol, namely **SYR-*Dec*** (Scheme 3).⁴⁹ Prior to copolymerization, we performed assays to test the reactivity of **SYR-*Dec*** in presence of GI and Zhan catalysts (ESI, Table S1). The obtained homopolymers exhibited molecular weights of 20.3 and 28.3 kDa when GI and Zhan catalysts were used, respectively, falling within the range of molecular weights previously obtained using HGII.⁴⁹ However, upon closer comparison, it was observed that the use of GI and Zhan resulted in higher dispersity, similar degradation temperature and lower T_g compared to HGII catalyst.



Scheme 3. ADMET co-polymerization of *Dec-BDMF* with *SYR-Dec*.

Therefore, GI was chosen as best performing catalyst to copolymerize *Dec-BDMF* and *SYR-Dec* at three different ratios, 10:90, 50:50 and 90:10, to produce polymers **P1**, **P2** and **P3**, respectively. ^1H NMR analysis revealed that both monomers were fully incorporated into the polymer, as evidenced by the maintenance of the corresponding ratios in the final copolymer (Figure 6). As expected, the T_g values increased significantly with a higher number of aromatic moieties (Figure 7). Similar molecular weight and dispersity were recorded for **P1** compared to the *SYR-dec* homopolymer. Copolymer **P3** also exhibited a SEC profile comparable to *Dec-BDMF*-derived polymer. Nevertheless, the increased dispersity (2.3) resulted in a broadening of the unimodal curve (Figure S11). In addition, DSC analysis revealed similar melting and crystallization transition as for *Dec-BDMF*-derived polymer (Figure S20). On the contrary, **P2** was amorphous (Figure S12) and a higher molecular weight was recorded, but with an increased dispersity, resulting in an intermediate value of M_n when compared with the homopolymers. These novel copolymers exhibited higher thermal stability (> 310 °C) in comparison to homopolymers derived from **BHMF**. TGA traces (Figures S13, S17 and S21) revealed only single-step degradation, providing support for the successful formation of copolymers.

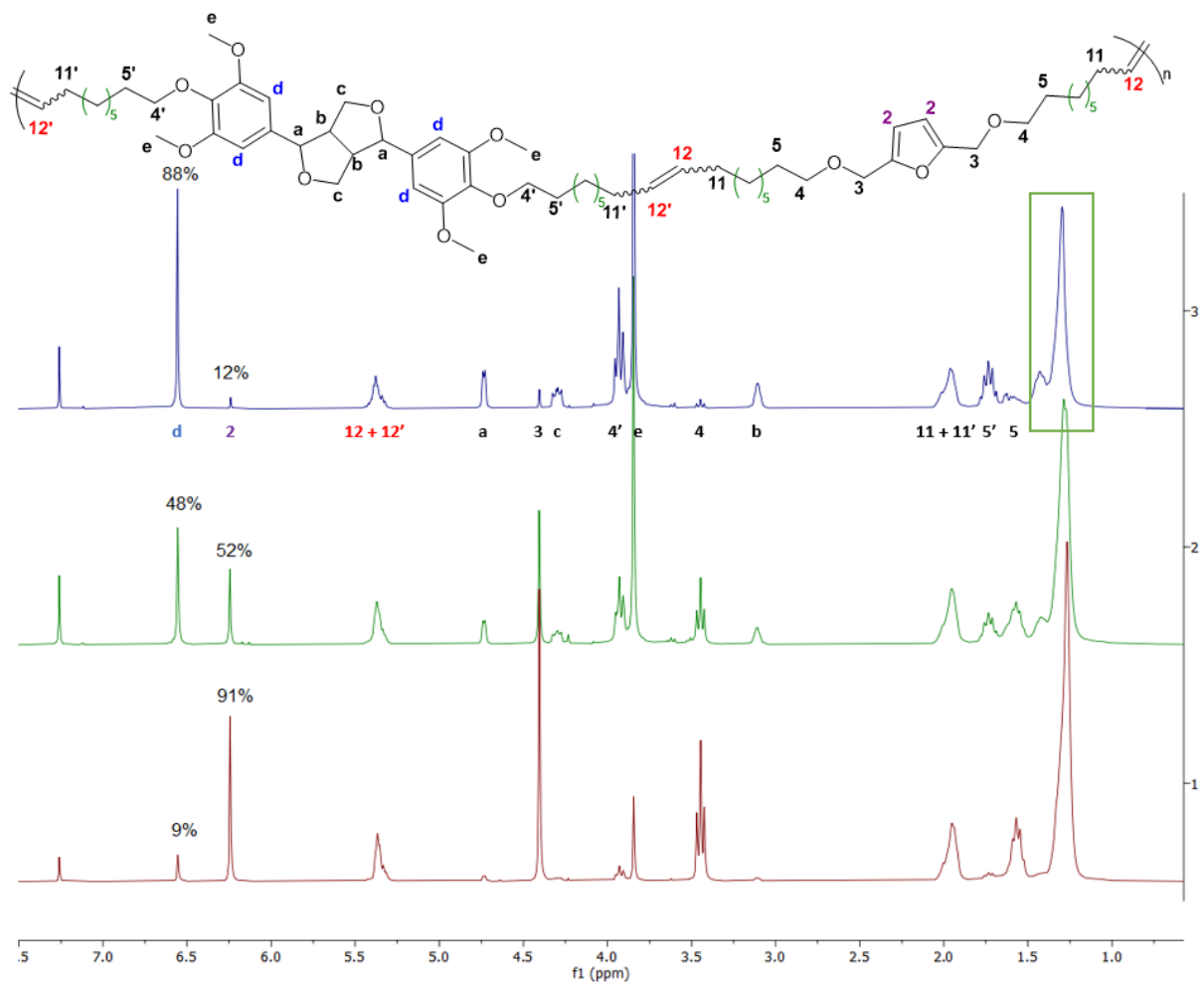


Figure 6. $^1\text{H-NMR}$ spectra of **P1** (blue), **P2** (green) and **P3** (red).

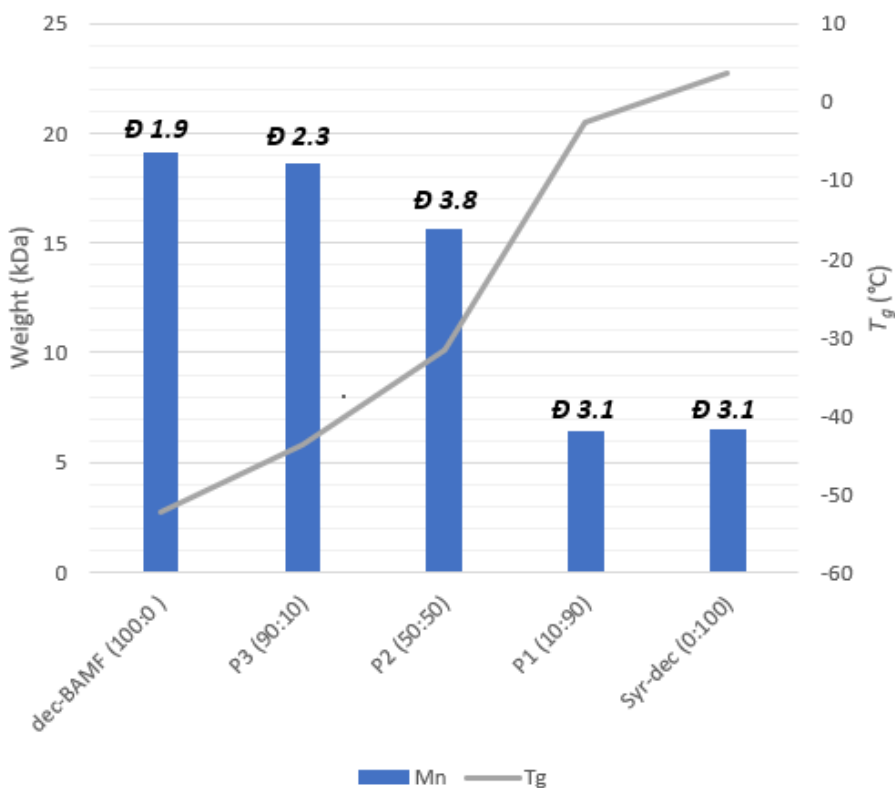


Figure 7. Results of copolymerization between *Dec-BDMF* and *SYR-Dec* in comparison with homopolymers using 1.0 mol% of GI catalyst, 2.0 mol% benzoquinone at 80 °C and 25 mbar.

3. Conclusion

The novel α,ω -dienes *Hex-BDMF* and *Dec-BDMF*, synthesized through the reaction of **BHMF** with hex-5-enol and dec-9-enol, respectively, were successfully subjected to ADMET polymerization, yielding bio-based furanic polyethers. Among the seven ruthenium-based catalysts tested, it was intriguing to observe that the least expensive Grubbs 1st generation catalyst (GI) outperformed the others. It produced polymers with higher molecular weights, reaching up to 43.2 kDa, and demonstrated good thermal stability (>200 °C). Remarkably, GI maintained its catalytic activity in the presence of three green solvents CyreneTM, DMI and GVL, with CyreneTM proving to be the most effective.

Additionally, the ADMET copolymerization of *Dec*-**BDMF** with **SYR**-Dec was accomplished, resulting in complete incorporation of both monomers into the final copolymers. By adjusting the relative amounts of the aromatic **SYR**-Dec monomer, it was possible to achieve copolymers with higher glass transition temperatures. In particular, the low T_g of homopolymers (< -50 °C) was increased up to -2.7 °C in copolymers containing up to 90% of **SYR**-Dec. These results highlight the potential of using 5-hydroxymethylfurfural derivatives such as **BHMF** as renewable platform molecule for polymer production *via* acyclic diene metathesis polymerization.

4. Experimental Section

4.1. General

All the reagents and solvents were purchased from Sigma-Aldrich and employed without any further purification. Purolite-type catalysts were kindly provided by Purolite®. All the solid heterogeneous catalysts were dried in the oven at 100 °C overnight before use. Reactions were conducted in a silicon oil bath or in a Drysyn at the required temperature. Reactions have been monitored by GC-MS Agilent Technologies (GC System 6890 N; Agilent Technologies Mass Selective Detector 5973) with a silica column (HP-5MS). Compounds have been injected through a Hamilton micro-syringe (10 μ L). NMR spectra were acquired through a spectrometer Bruker 400 MHz in $CDCl_3$ for monomers. Polymerizations were conducted under a controlled vacuum using a vacuubrand pump PC3001 vario^{Pro} and dried using a vacuubrand RZ 2.5. Polymers were analyzed through NMR using a Bruker Fourier 300. 1H NMR spectra were recorded at 300 MHz and were calibrated with a residual peak of $CDCl_3$ at 7.26 ppm. ^{13}C NMR spectra were recorded at 75 MHz and were calibrated on $CDCl_3$ peak at 77.16 ppm. Assignments were made using 2D experiments. Gel permeation chromatography (GPC) on an Agilent

Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector and two PLgel columns (5 μm MIXED-D 300 x 7.5 mm) using HPLC grade THF as the mobile layer at a flow rate of 1.0 mL/min at 50 $^{\circ}\text{C}$. Calibration was performed with polystyrene standards from Agilent Technologies.

Thermogravimetric Analysis (TGA) was measured with a TGA Q500 (TA Instruments). 5 to 10 mg of dried sample was equilibrated at 50 $^{\circ}\text{C}$ for 5 min and was flushed with highly pure nitrogen gas. All the experiments were performed with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ up to 500 $^{\circ}\text{C}$. Differential Scanning Calorimetry (DSC) was performed with a DSC Q20 (TA Instruments). 5 to 10 mg of sample were placed in a sealed pan, flushed with highly pure nitrogen gas and passed through a heat-cool-heat cycle at 2 $^{\circ}\text{C}/\text{min}$ in a temperature range of -80 $^{\circ}\text{C}$ to 100 $^{\circ}\text{C}$. Three heat/cool cycles were done for each sample, where the last two cycles were dedicated to analyzing the heat flow of the sample after being cooled in controlled conditions. The T_g values recorded herein are those obtained from the third cycle.

4.2. Monomers synthesis

2,5-bis((allyloxy)methyl)furan (*All-BDFM*)

2,5-Bis((allyloxy)methyl)furan was synthesized accordingly to a previously reported synthetic procedure.⁴¹ Briefly, to a solution of **BMHF** (0.5 g, 3.90 mmol) in allyl alcohol (30 mL, 0.51 mol), Purolite CT269DR (50 mg) was added and the mixture was allowed to react under stirring at 40 $^{\circ}\text{C}$ for 24 h. Then, the mixture was filtered through a celite pad and the solvent was evaporated under vacuum to give a crude brown oil. Purification by filtration on neutral aluminum oxide, using a mixture of Hex:EtOAc (from 95:5 to 80:20) as eluent, gave the desired compound in 57% yield (0.46 g) as a clear oil.

^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 6.29 (s, 2H), 5.99-5.89 (m, 2H) 5.34-5.29 (m, 2H), 5.24-5.21 (m, 2H), 4.46 (s, 4H), 4.06-4.04 (m, 4H).

^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) = 152.1 (2C), 134.4 (2C), 117.5 (2C), 110.0 (2C), 71.0 (2C), 64.0 (2C).

Hex-5-en-1-yl 4-methylbenzenesulfonate 1

TsCl (14.0 g, 73.2 mmol) was slowly added portion wise to a stirred and ice-cooled solution of hex-5-en-1-ol (6.6 g, 66.5 mmol), DMAP (4.1 g, 33.3 mmol) and Et_3N (8.8 g, 86.5 mmol) in DCM (100 mL) and left stirring overnight. Then, an additional 50 mL of DCM and 50 mL of distilled water were added to the reaction mixture. The reaction mixture was neutralized with acetic acid and transferred to a separatory funnel and washed with fresh water (3 x 50 mL). The organic layer was recovered, dried over anhydrous Na_2SO_4 , filtered on a pad of silica and celite before being concentrated. The product was recovered as a pale-yellow oil with a yield of 80% (13.3 g).

^1H -NMR (400 MHz, CDCl_3) δ ppm: 7.80 (d, 2H), 7.36 (d, 2H), 5.78 – 5.76 (m, 1H), 4.99 - 4.93 (m, 2H), 4.04 (t, 2H), 2.46 (s, 3H), 2.04 – 1.98 (m, 2H), 1.70 – 1.63 (m, 2H), 1.46 – 1.38 (m, 2H).

The spectroscopic data were consistent with those reported in the literature.⁵¹

Dec-9-en-1-yl 4-methylbenzenesulfonate 2

TsCl (12.2 g, 63.8 mmol) was slowly added portion wise to a stirred and ice-cooled solution of dec-9-en-1-ol (9 g, 58 mmol), DMAP (3.5 g, 29.0 mmol) and Et_3N (7.7 g, 75.4 mmol) in DCM

(100 mL) and left stirring overnight. Then, an additional 50 mL of DCM and 50 mL of distilled water were added to the reaction mixture. The reaction mixture was neutralized with acetic acid and transferred to a separatory funnel and washed with fresh water (3 x 50 mL). The organic layer was recovered, dried over anhydrous Na₂SO₄ and filtered on a pad of silica and celite, before being concentrated. The product was recovered as a pale-yellow oil that solidified in the fridge with a yield of 90% (16.2 g).

¹H-NMR (400 MHz, CDCl₃) δ ppm: 7.80 (d, 2H), 7.36 (d, 2H), 5.86 – 5.67 (m, 1H), 5.02 - 4.93 (m, 2H), 4.03 (t, 2H), 2.46 (s, 3H), 2.07 – 2.01 (m, 2H), 1.68 – 1.61 (m, 2H), 1.38 – 1.25 (m, 10H).

The spectroscopic data were consistent with those reported in the literature.⁵²

2,5-bis((hex-5-en-1-yloxy)methyl)furan (*Hex-BDMF*)

To **BHMF** (2.0 g, 15.6 mmol) in DMF (100 mL) was added *t*-BuONa (4.5 g, 46.8 mmol) in portion at 0 °C. After 15 min, tosylated alcohol (2.2 eq. mol) was added. Then, the mixture reaction was warmed at 110 °C under nitrogen flow and monitored by TLC. When **BHMF** was fully consumed, the mixture was cooled to room temperature. The reaction mixture was diluted in 100 mL of DCM and transferred to a separating funnel. After brine wash (x3) to remove most of DMF, the organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified with a chromatographic column using a mixture of Hex:Et₂O (from 96/4 to 9/1). The product was recovered in 49% yield (2.27 g) as a pale-yellow oil that solidified in the fridge.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 6.27 (s, 2H), 5.87 – 5.76 (m, 2H), 5.04 – 4.94 (m, 4H), 4.44 (s, 4H); 3.49 (t, 4H), 2.10 – 2.05 (m, 4H), 1.66 – 1.59 (m, 4H), 1.50 – 1.43 (m, 4H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 152.3, 138.7, 114.5, 109.6, 70.2, 64.9, 33.5, 29.1, 25.4.

HRMS: m/z $[\text{M}+\text{Na}]^+$ calc. for $[\text{C}_{18}\text{H}_{28}\text{O}_3\text{Na}]^+$: 315.1931; found: 315.1925.

2,5-bis((dec-9-en-1-yloxy)methyl)furan (*Dec-BDMF*)

To BDMF (3.0 g, 23.4 mmol) in DMF (100 mL) was added *t*-BuONa (6.8 g, 70.2 mmol) in portion at 0 °C. After 15 min, tosylated alcohol (2.2 eq. mol) were added. Then, the mixture reaction was warmed at 110 °C under nitrogen flow and monitored by TLC. When BDMF was fully consumed, the mixture was cooled to room temperature. The reaction mixture was diluted in 100 mL of DCM and transferred to a separating funnel. After brine wash (x3) to remove most of DMF, the organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was purified with a chromatographic column. The residue was purified with a chromatographic column using a mixture of Hex:Et₂O (from 96/4 to 9/1). The product was recovered in 48% yield (4.60 g) as a pale-yellow oil that solidified in the fridge.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ ppm: 6.27 (s, 2H), 5.88 – 5.78 (m, 2H), 5.03 – 4.93 (m, 4H), 4.44 (s, 4H); 3.48 (t, 4H), 2.08 – 2.03 (m; 4H), 1.64 – 1.56 (m; 4H), 1.39 – 1.29 (m, 20H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ ppm: 152.3, 139.2, 114.1, 109.6, 70.5, 64.9, 33.8, 29.6, 29.4, 29.1, 28.9, 26.1.

HRMS: m/z $[\text{M}+\text{Na}]^+$ calc. for $[\text{C}_{26}\text{H}_{44}\text{O}_3\text{Na}]^+$: 427.3183; found: 427.3174.

4.3. ADMET Polymerization

General procedure for solvent-free ADMET polymerization

243.0 mg of *Dec-BDMF* or 175.0 mg of *Hex-BDMF* (0.6 mmol) and 1.3 mg of *p*-benzoquinone (2mol%) were placed at 80 °C under reduced pressure (25 mbar). Then catalyst was added (1 mol%). Aliquots were taken at different time intervals, dissolved in CDCl₃ and analyzed through ¹H NMR to monitor the reaction. At the end of the reaction, 2 mL of a 10%v/v solution of ethyl vinyl ether in THF was added to stop the reaction.

General procedure for in-solvent ADMET polymerization

At the monomers and *p*-benzoquinone was added 150 or 300 μL of the desired solvent to achieve a monomers concentration of 4 or 2 mol/L. Reaction media was heated up at 80 °C under reduced pressure (25 or 50 mbar). Then GI catalyst was added (4.94 mg, 1 mol%). Aliquots were taken at different time intervals, dissolved in CDCl₃ and analyzed through ¹H NMR to monitor the reaction. At the end of the reaction, 2 mL of a 10%v/v solution of ethyl vinyl ether in THF was added to stop the reaction.

The crude polymer was adsorbed on Celite435®. The solid powder was rinsed with ethanol to eliminate catalyst and solvent, then with dichloromethane to recover the polymer.

Hex-BDMF-derived polymers

¹H NMR (300 MHz, Chloroform-*d*) δ 6.24 (s, 2H, H2), 5.46 – 5.27 (m, 2H, H8), 4.40 (s, 4H, H3), 3.45 (td, *J* = 6.6, 1.2 Hz, 4H, H4), 1.98 (dt, *J* = 11.4, 6.6 Hz, 4H, H7), 1.58 (ddt, *J* = 12.7, 9.0, 4.8 Hz, 4H, H5), 1.46 – 1.30 (m, 4H, H6).

^{13}C NMR (75 MHz, CDCl_3) δ 152.4 (C1), 130.4 (C8), 129.9 (C8'), 109.8 (C2), 70.4 (C4), 65.0 (C3), 32.5 (C7), 29.4+29.2 (C5), 27.1 (C7'), 26.3+26.2 (C6).

Dec-BDMF-derived polymers

^1H NMR (300 MHz, Chloroform-*d*) δ 6.24 (s, 2H, H2), 5.37 (ddd, $J = 5.3, 3.7, 1.5$ Hz, 2H, H12), 4.41 (s, 4H, H3), 3.45 (t, $J = 6.7$ Hz, 4H, H4), 1.96 (t, $J = 6.4$ Hz, 4H, H11), 1.57 (t, $J = 7.1$ Hz, 4H, H5), 1.45 – 1.02 (m, 20H, H6-7-8-9-10).

^{13}C NMR (75 MHz, CDCl_3) δ 152.4 (C1), 130.5 (C12), 130.0 (C12'), 109.7 (C2), 70.6 (C4), 65.0 (C3), 32.7 (C11), 29.9-29.3 (C5-7-8-9-10), 27.3 (C11'), 26.2 (C6).

General procedure for solvent-free ADMET co-polymerization with SYR-*Dec*

Dec-BDMF and *SYR-Dec* were mixed in molar ratio 10:90, 50:50 or 90:10 (total 0.6 mmol), then 1.3 mg of *p*-benzoquinone (2 mol%) was added. The reaction media was placed at 80 °C under reduced pressure (25 mbar). Then GI catalyst was added (4.94 mg, 1 mol%). Aliquots were taken at different time intervals, dissolved in CDCl_3 and analyzed through ^1H NMR to monitor the reaction. At the end of the reaction, 2 mL of a 10%v/v solution of ethyl vinyl ether in THF was added to the reaction medium. The crude polymer was concentrated on rotavapor then dried under high vacuum.

P1 from 10:90 *Dec-BDMF*:*Syr-Dec* mixture

^1H NMR (300 MHz, CDCl_3) δ 6.56 (s, 2.50H, Hd), 6.24 (s, 0.12H, H2), 5.42 – 5.29 (m, 2.00H, H12 and 12'), 4.73 (d, $J = 3.9$ Hz, 1.23H, Ha), 4.40 (s, 0.24H, H3), 4.36 – 4.24 (m, 0.72H, Hc), 3.93 (t, $J = 6.9$ Hz, 4.50H, H4'), 3.84 (s, 8.22H, He), 3.45 (t, $J = 6.7$ Hz, 0.24H, H4), 3.13 – 3.07

(m, 1.37H, Hb), 2.11 – 1.86 (m, 4.38H, H11 and 11'), 1.81 – 1.66 (m, 3.12H, H5'), 1.66 – 1.48 (m, 0.80H, H5), 1.49 – 1.16 (m, 20.12H, H6-10 and 6'-10').

¹³C NMR (75 MHz, CDCl₃) δ 153.8, 137.1, 136.5, 130.5, 130.0, 103.2, 86.2, 73.7, 72.1, 56.4, 54.5, 32.8, 30.2, 29.8, 29.6, 29.6, 29.4, 29.3, 27.4, 26.0.

P2 from 50:50 *Dec-BDMF:Syr-Dec* mixture

¹H NMR (300 MHz, CDCl₃) δ 6.55 (s, 1.43H, Hd), 6.24 (s, 0.82H, H2), 5.54 – 5.24 (m, 2.00H H12 and 12'), 4.73 (d, *J* = 3.9 Hz, 0.68H, Ha), 4.41 (s, 1.64H, H3), 4.36 – 4.26 (m, 0.63H, Hc), 3.98 – 3.88 (m, 2.31H, H4' and He), 3.45 (t, *J* = 6.7 Hz, 1.80H, H4), 3.22 – 2.97 (m, 0.75H, Hb), 2.12 – 1.85 (m, 4.32H, H11 and 11'), 1.79 – 1.68 (m, 1.61H, H5'), 1.60 – 1.52 (m, 3.09H, H5), 1.48 – 1.05 (m, 20.72H, H6-10 and 6'-10').

¹³C NMR (75 MHz, CDCl₃) δ 153.8, 152.4, 137.0, 136.5, 130.5, 130.0, 109.8, 103.1, 86.2, 73.7, 72.1, 70.6, 65.0, 56.4, 54.4, 32.8, 30.2, 29.8, 29.6, 29.3, 27.4, 26.2, 26.0.

P3 from 90:10 *Dec-BDMF:Syr-Dec* mixture

¹H NMR (300 MHz, CDCl₃) δ 6.55 (s, 0.34H, Hd), 6.24 (s, 1.75H, H2), 5.47 – 5.20 (m, 2.00H H12 and 12'), 4.73 (d, *J* = 3.8 Hz, 0.15H, Ha), 4.41 (s, 3.61H, H3), 4.02 – 3.88 (m, 0.52H, Hc and H4'), 3.84 (s, 1.02H, He), 3.45 (t, *J* = 6.7 Hz, 3.56H, H4), 3.20 – 2.99 (m, 0.15H, Hb), 2.20 – 1.83 (m, 4.32H, H11 and 11'), 1.83 – 1.64 (m, 0.20H, H5'), 1.64 – 1.46 (m, 3.80H, H5), 1.46 – 1.07 (m, 20.93H, H6-10 and 6'-10').

¹³C NMR (75 MHz, CDCl₃) δ 153.8, 152.4, 136.9, 136.5, 130.5, 130.0, 109.8, 103.1, 73.7, 70.6, 65.0, 56.3, 54.4, 32.7, 30.2, 29.9, 29.8, 29.6, 29.6, 29.4, 29.4, 29.3, 27.3, 26.2, 26.0.

ASSOCIATED CONTENT

Supporting Information.

A supporting information file is available free of charge (pdf). It contains:

NMR spectra and DSC thermograms of the polymers and a table summarizing ADMET polymerization using Syr-Dec as co-monomer.

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REFERENCES

- (1) Hou, Q.; Qi, X.; Zhen, M.; Qian, H.; Nie, Y.; Bai, C.; Zhang, S.; Bai, X.; Ju, M. Biorefinery Roadmap Based on Catalytic Production and Upgrading 5-Hydroxymethylfurfural. *Green Chemistry* **2021**, *23* (1), 119–231. <https://doi.org/10.1039/D0GC02770G>.
- (2) Musolino, M.; Andraos, J.; Aricò, F. An Easy Scalable Approach to HMF Employing DMC as Reaction Media: Reaction Optimization and Comparative Environmental Assessment. *ChemistrySelect* **2018**, *3* (8), 2359–2365. <https://doi.org/10.1002/slct.201800198>.
- (3) 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. *Chem Soc Rev* **2020**, *49* (13), 4273–4306. <https://doi.org/10.1039/D0CS00041H>.
- (4) Menegazzo, F.; Ghedini, E.; Signoretto, M. 5-Hydroxymethylfurfural (HMF) Production from Real Biomasses. *Molecules* **2018**, *23* (9), 2201. <https://doi.org/10.3390/molecules23092201>.
- (5) Yu, I. K. M.; Tsang, D. C. W. Conversion of Biomass to Hydroxymethylfurfural: A Review of Catalytic Systems and Underlying Mechanisms. *Bioresour Technol* **2017**, *238*, 716–732. <https://doi.org/10.1016/j.biortech.2017.04.026>.
- (6) Bicker, M.; Hirth, J.; Vogel, H. Dehydration of Fructose to 5-Hydroxymethylfurfural in Sub- and Supercritical Acetone. *Green Chemistry* **2003**, *5* (2), 280–284. <https://doi.org/10.1039/b211468b>.
- (7) Dashtban, M.; Gilbert, A.; Fatehi, P. Recent Advancements in the Production of Hydroxymethylfurfural. *RSC Adv.* **2014**, *4* (4), 2037–2050. <https://doi.org/10.1039/C3RA45396K>.
- (8) Dick, G. R.; Frankhouser, A. D.; Banerjee, A.; Kanan, M. W. A Scalable Carboxylation Route to Furan-2,5-Dicarboxylic Acid. *Green Chemistry* **2017**, *19* (13), 2966–2972. <https://doi.org/10.1039/C7GC01059A>.
- (9) Chen, G.; van Straalen, N. M.; Roelofs, D. The Ecotoxicogenomic Assessment of Soil Toxicity Associated with the Production Chain of 2,5-Furandicarboxylic Acid (FDCA), a Candidate Bio-Based Green Chemical Building Block. *Green Chemistry* **2016**, *18* (16), 4420–4431. <https://doi.org/10.1039/C6GC00430J>.
- (10) Aricò, F. Synthetic Approaches to 2,5-Bis(Hydroxymethyl)Furan (BHMF): A Stable Bio-Based Diol. *Pure and Applied Chemistry* **2021**, *93* (5), 551–560. <https://doi.org/10.1515/pac-2021-0117>.
- (11) Fang, W.; Riisager, A. Recent Advances in Heterogeneous Catalytic Transfer Hydrogenation/Hydrogenolysis for Valorization of Biomass-Derived Furanic

- Compounds. *Green Chemistry* **2021**, *23* (2), 670–688. <https://doi.org/10.1039/D0GC03931D>.
- (12) Bragato, N.; Fiorani, G. Cyclic Organic Carbonates from Furanics: Opportunities and Challenges. *Curr Opin Green Sustain Chem* **2021**, *30*, 100479. <https://doi.org/10.1016/j.cogsc.2021.100479>.
- (13) de la Cruz-Martínez, F.; Martínez de Sarasa Buchaca, M.; Martínez, J.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Rodríguez-Diéguez, A.; Castro-Osma, J. A.; Lara-Sánchez, A. Synthesis of Bio-Derived Cyclic Carbonates from Renewable Resources. *ACS Sustain Chem Eng* **2019**, *7* (24), 20126–20138. <https://doi.org/10.1021/acssuschemeng.9b06016>.
- (14) Saini, Ms. K.; Kumar, S.; Li, H.; Babu, S. A.; Saravanamurugan, S. Advances in the Catalytic Reductive Amination of Furfural to Furfural Amine: The Momentous Role of Active Metal Sites. *ChemSusChem* **2022**, *15* (7). <https://doi.org/10.1002/cssc.202200107>.
- (15) Sathicq, A. G.; Annatelli, M.; Abdullah, I.; Romanelli, G.; Aricò, F. Alkyl Carbonate Derivatives of Furanics: A Family of Bio-Based Stable Compounds. *Sustain Chem Pharm* **2021**, *19*, 100352. <https://doi.org/10.1016/j.scp.2020.100352>.
- (16) Casanova, O.; Iborra, S.; Corma, A. Chemicals from Biomass: Etherification of 5-Hydroxymethyl-2-Furfural (HMF) into 5,5'-(Oxy-Bis(Methylene))Bis-2-Furfural (OBMF) with Solid Catalysts. *J Catal* **2010**, *275* (2), 236–242. <https://doi.org/10.1016/j.jcat.2010.08.002>.
- (17) Annatelli, M.; Trapasso, G.; Dalla Torre, D.; Pietrobon, L.; Redolfi-Bristol, D.; Aricò, F. A Green Synthesis of 5,5'-[Oxybis(Methylene)]Bis-2-Furfural: From By-Product to Attractive Bio-Based Platform Chemical. **2022**. <https://doi.org/10.1002/adsu.202200297>.
- (18) de Jong, E.; Dam, M. A.; Sipos, L.; Gruter, G.-J. M. Furandicarboxylic Acid (FDCA), A Versatile Building Block for a Very Interesting Class of Polyesters. In *Biobased Monomers, Polymers and Materials*; ACS Symposium Series: Whashington DC, USA, 2012; Vol. 1105, pp 1–13. <https://doi.org/10.1021/bk-2012-1105.ch001>.
- (19) Guillaume, L.; Marshall, A.; Niessen, N.; Ni, P.; Gauvin, R. M.; Thomas, C. M. Multicatalysis from Renewable Resources: A Direct Route to Furan-Based Polyesters. *Green Chemistry* **2021**, *23* (18), 6931–6935. <https://doi.org/10.1039/D1GC01889B>.
- (20) Post, C.; Maniar, D.; Voet, V. S. D.; Folkersma, R.; Loos, K. Biobased 2,5-Bis(Hydroxymethyl)Furan as a Versatile Building Block for Sustainable Polymeric Materials. *ACS Omega* **2023**, *8* (10), 8991–9003. <https://doi.org/10.1021/acsomega.2c07629>.

- (21) Oh, C.; Choi, E. H.; Choi, E. J.; Premkumar, T.; Song, C. Facile Solid-State Mechanochemical Synthesis of Eco-Friendly Thermoplastic Polyurethanes and Copolymers Using a Biomass-Derived Furan Diol. **2020**. <https://doi.org/10.1021/acssuschemeng.9b06944>.
- (22) Zhang, L.; Michel, F. C.; Co, A. C. Nonisocyanate Route to 2,5-Bis(Hydroxymethyl)Furan-Based Polyurethanes Crosslinked by Reversible Diels-Alder Reactions. **2019**. <https://doi.org/10.1002/pola.29418>.
- (23) Cousin, T.; Galy, J.; Rousseau, A.; Dupuy, J. Synthesis and Properties of Polyamides from 2,5-Furandicarboxylic Acid. *J Appl Polym Sci* **2018**, *135* (8), 45901. <https://doi.org/10.1002/app.45901>.
- (24) Jiang, Y.; Maniar, D.; Woortman, A. J. J.; Loos, K. Enzymatic Synthesis of 2,5-Furandicarboxylic Acid-Based Semi-Aromatic Polyamides: Enzymatic Polymerization Kinetics, Effect of Diamine Chain Length and Thermal Properties. *RSC Adv* **2016**, *6* (72), 67941–67953. <https://doi.org/10.1039/C6RA14585J>.
- (25) Huang, W.; Hu, X.; Zhai, J.; Zhu, N.; Guo, K. Biorenewable Furan-Containing Polyamides. *Materials Today Sustainability* **2020**, *10*, 100049. <https://doi.org/10.1016/j.mtsust.2020.100049>.
- (26) Eid, N.; Ameduri, B.; Boutevin, B. Synthesis and Properties of Furan Derivatives for Epoxy Resins. *ACS Sustain Chem Eng* **2021**, *9* (24), 8018–8031. <https://doi.org/10.1021/acssuschemeng.0c09313>.
- (27) Mutlu, H.; de Espinosa, L. M.; Meier, M. A. R. Acyclic Dienemetathesis: A Versatile Tool for the Construction of Defined Polymer Architectures. *Chem. Soc. Rev.* **2011**, *40* (3), 1404–1445. <https://doi.org/10.1039/B924852H>.
- (28) Atallah, P.; Wagener, K. B.; Schulz, M. D. ADMET: The Future Revealed. *Macromolecules*. June 25, 2013, pp 4735–4741. <https://doi.org/10.1021/ma400067b>.
- (29) Kreye, O.; Tóth, T.; Meier, M. A. R. Copolymers Derived from Rapeseed Derivatives via ADMET and Thiol-Ene Addition. *Eur Polym J* **2011**, *47* (9), 1804–1816. <https://doi.org/10.1016/j.eurpolymj.2011.06.012>.
- (30) Firdaus, M.; Meier, M. A. R. Renewable Co-Polymers Derived from Vanillin and Fatty Acid Derivatives. *Eur Polym J* **2013**, *49* (1), 156–166. <https://doi.org/10.1016/j.eurpolymj.2012.10.017>.
- (31) Mutlu, H.; Meier, M. A. R. Unsaturated PA X₂₀ from Renewable Resources via Metathesis and Catalytic Amidation. *Macromol Chem Phys* **2009**, *210* (12), 1019–1025. <https://doi.org/10.1002/macp.200900045>.
- (32) Lebarbé, T.; Neqal, M.; Grau, E.; Alfos, C.; Cramail, H. Branched Polyethylene Mimicry by Metathesis Copolymerization of Fatty Acid-Based α,ω -Dienes. *Green Chem.* **2014**, *16* (4), 1755–1758. <https://doi.org/10.1039/C3GC42280A>.

- (33) Dannecker, P.; Biermann, U.; Sink, A.; Bloesser, F. R.; Metzger, J. O.; Meier, M. A. R. Fatty Acid-Derived Aliphatic Long Chain Polyethers by a Combination of Catalytic Ester Reduction and ADMET or Thiol- Ene Polymerization. *Macromol Chem Phys* **2018**, 1800440. <https://doi.org/10.1002/macp.201800440>.
- (34) Shearouse, W. C.; Lillie, L. M.; Reineke, T. M.; Tolman, W. B. Sustainable Polyesters Derived from Glucose and Castor Oil: Building Block Structure Impacts Properties. *ACS Macro Lett* **2015**, 4 (3), 284–288. <https://doi.org/10.1021/acsmacrolett.5b00099>.
- (35) Le, D.; Samart, C.; Kongparakul, S.; Nomura, K. Synthesis of New Polyesters by Acyclic Diene Metathesis Polymerization of Bio-Based α,ω -Dienes Prepared from Eugenol and Castor Oil (Undecenoate). *RSC Adv* **2019**, 9 (18), 10245–10252. <https://doi.org/10.1039/C9RA01065C>.
- (36) Barbara, I.; Flourat, A. L.; Allais, F. Renewable Polymers Derived from Ferulic Acid and Biobased Diols via ADMET. *Eur Polym J* **2015**, 62, 236–243. <https://doi.org/10.1016/j.eurpolymj.2014.11.035>.
- (37) Zeaiter, N.; Fadlallah, S.; Flourat, A. L.; Allais, F. Aliphatic-Aromatic Polyesters from Naturally Occurring Sinapic Acid through Acyclic-Diene Metathesis Polymerization in Bulk and Green Solvent Cyrene. *ACS Sustain Chem Eng* **2022**, 10 (51), 17336–17345. <https://doi.org/10.1021/acssuschemeng.2c05901>.
- (38) Nomura, K.; Chaijaroen, P.; Abdellatif, M. M. Synthesis of Biobased Long-Chain Polyesters by Acyclic Diene Metathesis Polymerization and Tandem Hydrogenation and Depolymerization with Ethylene. *ACS Omega* **2020**, 5 (29), 18301–18312. <https://doi.org/10.1021/acsomega.0c01965>.
- (39) Lillie, L. M.; Tolman, W. B.; Reineke, T. M. Structure/Property Relationships in Copolymers Comprising Renewable Isosorbide, Glucarodilactone, and 2,5-Bis(Hydroxymethyl)Furan Subunits. *Polym Chem* **2017**, 8 (24), 3746–3754. <https://doi.org/10.1039/C7PY00575J>.
- (40) Trapasso, G.; Mazzi, G.; Chícharo, B.; Annatelli, M.; Dalla Torre, D.; Arico, F. Multigram Synthesis of Pure HMF and BHMF. *Cite This: Org. Process Res. Dev* **2022**. <https://doi.org/10.1021/acs.oprd.2c00196>.
- (41) Musolino, M.; Ginés-Molina, M. J.; Moreno-Tost, R.; Aricò, F. Purolite-Catalyzed Etherification of 2,5-Bis(Hydroxymethyl)Furan: A Systematic Study. *ACS Sustain Chem Eng* **2019**, 7 (12), 10221–10226. <https://doi.org/10.1021/acssuschemeng.9b01413>.
- (42) Vlaminck, L.; Lingier, S.; Hufendiek, A.; du Prez, F. E. Lignin Inspired Phenolic Polyethers Synthesized via ADMET: Systematic Structure-Property Investigation. *Eur Polym J* **2017**, 95, 503–513. <https://doi.org/10.1016/j.eurpolymj.2017.08.042>.
- (43) Schmidt, B. Catalysis at the Interface of Ruthenium Carbene and Ruthenium Hydride Chemistry: Organometallic Aspects and Applications to Organic

- Synthesis. *European J Org Chem* **2004**, 2004 (9), 1865–1880. <https://doi.org/10.1002/ejoc.200300714>.
- (44) Del Vecchio, A.; Smallman, H. R.; Morvan, J.; McBride, T.; Browne, D. L.; Mauduit, M. Challenges Arising from Continuous- Flow Olefin Metathesis. *Angewandte Chemie International Edition* **2022**, 61 (47). <https://doi.org/10.1002/anie.202209564>.
- (45) Bell, M.; Hester, H. G.; Gallman, A. N.; Gomez, V.; Pribyl, J.; Rojas, G.; Riegger, A.; Weil, T.; Watanabe, H.; Chujo, Y.; Wagener, K. B. Bulk Acyclic Diene Metathesis Polycondensation. *Macromol Chem Phys* **2019**, 220 (1900223), 1–5. <https://doi.org/10.1002/macp.201900223>.
- (46) Liu, S.; Yan, J.; Zhang, Q.; Yan, Y. Acyclic Diene Metathesis (ADMET) as Powerful Tool for Functional Polymers with Versatile Architectures. *Journal of Inorganic and Organometallic Polymers and Materials*. Springer September 1, 2022, pp 3368–3394. <https://doi.org/10.1007/s10904-022-02386-x>.
- (47) Lebarbé, T.; More, A. S.; Sane, P. S.; Grau, E.; Alfos, C.; Cramail, H. Bio-Based Aliphatic Polyurethanes Through ADMET Polymerization in Bulk and Green Solvent. *Macromol Rapid Commun* **2014**, 35 (4), 479–483. <https://doi.org/10.1002/marc.201300695>.
- (48) Pribyl, J.; Wagener, K. B.; Rojas, G. ADMET Polymers: Synthesis, Structure Elucidation, and Function. *Mater Chem Front* **2021**, 5 (1), 14–43. <https://doi.org/10.1039/D0QM00273A>.
- (49) Hollande, L.; Jaufurally, A. S.; Ducrot, P. H.; Allais, F. ADMET Polymerization of Biobased Monomers Deriving from Syringaresinol. *RSC Adv* **2016**, 6 (50), 44297–44304. <https://doi.org/10.1039/c6ra06348a>.
- (50) Moser, B. R.; Vermillion, K. E.; Banks, B. N.; Doll, K. M. Renewable Aliphatic Polyesters from Fatty Dienes by Acyclic Diene Metathesis Polycondensation. *JAACS, Journal of the American Oil Chemists' Society* **2020**, 97 (5), 517–530. <https://doi.org/10.1002/aocs.12338>.
- (51) Xu, J.; Fu, Y.; Luo, D.-F.; Jiang, Y.-Y.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. Copper-Catalyzed Trifluoromethylation of Terminal Alkenes through Allylic C–H Bond Activation. *J Am Chem Soc* **2011**, 133 (39), 15300–15303. <https://doi.org/10.1021/ja206330m>.
- (52) Fash, D. M.; Khmour, O. M.; Sahdeo, S. J.; Goldschmidt, R.; Jaruvangsanti, J.; Dey, S.; Arce, P. M.; Collin, V. C.; Cortopassi, G. A.; Hecht, S. M. Effects of Alkyl Side Chain Modification of Coenzyme Q 10 on Mitochondrial Respiratory Chain Function and Cytoprotection. *Bioorg Med Chem* **2013**, 21 (8), 2346–2354. <https://doi.org/10.1016/j.bmc.2013.01.075>.

SYNOPSIS

Bio-based α,ω -dienes derived from BHMF were efficiently polymerized through acyclic diene metathesis in various conditions affording poly(ether-alkenamer)s