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Renewable hydroxymethylfurfural epoxide and cyclic anhydride copolymerization: a green route to functional biobased polyesters

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The copolymerization of epoxides and cyclic anhydrides is a promising route for synthesizing polyesters with potential degradability and biocompatibility. In this study, a bio-based epoxy monomer derived from 5-hydroxymethylfurfural (5-HMF) copolymerized with cyclic anhydrides introduces aldehyde functionalities directly into the polyester backbone using a binary Cr(salen)Cl (**1**)/PPNCl catalytic system. The copolymerization with a broad range of renewable cyclic anhydrides and the use of propylene carbonate as a solvent make this process greener. Also, we highlighted the orthogonal post-polymerization modification (PPM) capabilities with poly(CFGE-*alt*-(*exo*-NA)) exploiting both aldehyde and alkene groups, demonstrating selective and independent aldehyde-to-imine and thiol-ene transformations in a one-pot dual PPM reaction. This methodology presents a sustainable pathway for bio-based polyester synthesis, enabling the tuning of material properties across diverse applications through a post-polymerization modification (PPM) approach.
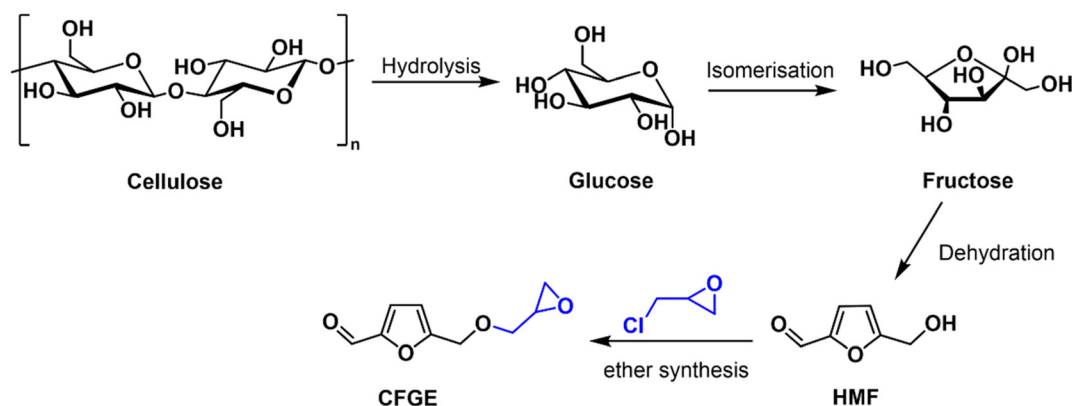
Introduction

Plastics continue to be an important class of consumable polymeric materials, with global demand continuing to rise steadily. From 1950 to 2015, the annual plastic production increased dramatically from 2 to 380 million metric tons (Mt), contributing to growing environmental pollution across natural ecosystems. This increased consumption is projected to reach more than 1100 Mt per year by 2050.[1,2] With growing concern over the environmental problem of plastic pollution, numerous efforts have been dedicated to replacing traditional petrochemical-based non-degradable polymers with bio-based degradable alternatives that offer desirable characteristics such as renewability and environmental friendliness.[3] In this context, polyesters from bio-based alternatives present an opportunity to develop a promising solution with potential degradability and biocompatibility.[4] Among them, the copolymerization of epoxides and cyclic anhydrides presents an attractive route for producing polyesters, specifically monomers derived from renewable sources.[5] In an effort to assist in this endeavour, we and several others have developed effective methods for the utilization of a wide range of biomass derivatives as a feedstock for the synthesis of polymers.[6] Despite sig-

nificant progress, the copolymerization of epoxides and cyclic anhydrides remains limited by the structural diversity of available monomers, particularly in the pursuit of functional polymers designed for post-synthetic modifications or curing applications. To date, post-functionalization strategies have predominantly involved utilizing an alkene functional group present in the polyester backbones.[7] In 2018, Coates and co-workers demonstrated for the first time the incorporation of aldehyde functionalities directly into the polyester backbone by employing vanillin glycidyl ether (VGE). They further expanded the versatility of the resulting polyester through orthogonal functionalization, applying sequential thiol-ene chemistry followed by Schiff base formation.[8] Since the pendant aldehyde functionality offers versatile opportunities to tune the properties of the resulting polyesters, due to its reactivity, it has been utilized as a functional handle in post-polymer modification processes.[9] In this regard, the exploration of renewable and readily accessible biosourced monomers for the synthesis of aldehyde functionalized polyesters remains a promising opportunity to enhance both sustainability and molecular versatility.

An interesting biosourced epoxy monomer can be derived from 5-hydroxymethylfurfural (5-HMF).[10] 5-HMF is widely recognized as a highly promising platform feedstock with a structure comprising a furan ring, an aldehyde group, and a hydroxymethyl group. This versatility offers remarkable and diverse reactivity, and so it has been called the "*sleeping giant*"

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Scheme 1 Conversion pathway from cellulose to the 5-HMF monomer.

in the field of intermediate chemicals from renewable feedstocks.[11] Hence, it has been extensively studied for its potential applications in the production of valuable chemicals, fuels, and materials.[12] 5-Hydroxymethylfurfural is typically produced *via* the acid-catalyzed dehydration of the C6 monosaccharide fructose. It can also be obtained in varying amounts from different monomeric C6 sugars through successive hydrolysis and dehydration processes involving polysaccharides such as cellulose (Scheme 1).[13] It has also been listed as one of the top potential platform chemicals from renewable feedstocks by the US Department of Energy.[14] Inspired by the potential of the biomass-derived platform molecule 5-HMF, we explored its use in the synthesis of an epoxy monomer designed for the production of polymers.[15] Herein, we present the polymerization of an HMF derived aldehyde functionalized epoxy monomer and cyclic anhydrides. This system facilitates the synthesis of aldehyde-active polyesters and supports orthogonal functionalization, expanding the scope of structural and functional tunability in these materials.

Results and discussion

In continuation of our significant interest in selectively producing degradable polymers from biomass based epoxides,[16] herein, we explored a 5-HMF derived epoxide monomer for its copolymerization with cyclic anhydrides. We have recently reported the successful multigram-scale synthesis of the biomass-based epoxy monomer CFGE, utilizing renewable 5-hydroxymethylfurfural (5-HMF) and epichlorohydrin (ECH).[15] The latter is also available from renewable resources. Firstly, the copolymerization was carried out between CFGE and phthalic anhydride (PA) using well known binary Cr(salen) Cl (1)/PPNCl as a catalyst system[17] at 90 °C in toluene and the results are given in Table 1. The use of this binary chromium (III) and onium salt catalysts has been shown in the past by us to be effective at performing copolymerization with anhydrides. As expected, the polymerization showed high activity
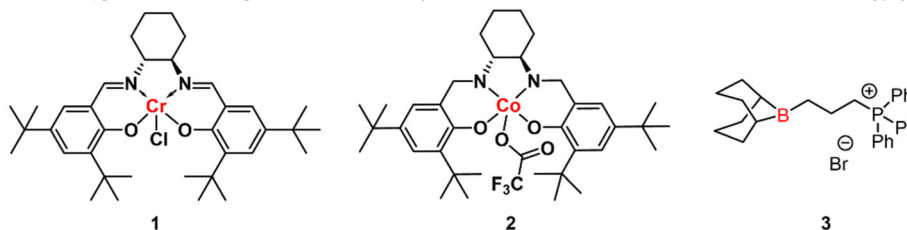
and selectivity towards the synthesis of poly(CFGE-*alt*-PA) with complete conversion in an hour, validating our initial choice of catalysts for this process. In pursuit of a greener approach, we investigated copolymerization using propylene carbonate (PC) as a solvent, thereby establishing a greener pathway for synthesizing functional biopolyesters.[18] Under similar conditions to those used with toluene as the solvent, complete conversion of the polyester was attained after 18 hours (entry 3). Increasing the temperature to 120 °C significantly accelerated the process, resulting in complete conversion within an hour. Next, to optimize the catalytic system comprising complex **1**, the corresponding binary cobalt based system (**2**) and the metal-free bifunctional boron based phosphonium salt (**3**) were evaluated,[19] displaying 67–69% conversion. The catalytic activity of complex **1** alone was investigated obtaining a lower conversion (70%) than that obtained along with PPNCl as a cocatalyst. On the other hand, a control reaction using only PPNCl as a catalyst showed 21% conversion, which indicates that the cocatalyst by itself could catalyze the reaction but less efficiently.

With the aim to broaden the substrate scope, copolymerization reactions involving various bio-based cyclic anhydrides with CFGE were evaluated (Fig. 1). Notably, monocyclic anhydrides can be synthesized *via* cyclization of dicarboxylic acids obtained from biomass, while bicyclic and tricyclic anhydrides are typically produced through Diels–Alder reactions involving maleic anhydride.[20] These dicarboxylic acids have been recognized by the U.S. Department of Energy as among the most promising platform chemicals derived from renewable feedstocks.[14] This enabled the synthesis of a broad range of renewable polyesters with diverse structural and electronic characteristics. The results are summarized in Table 2. In all cases, high selectivity toward the formation of the corresponding polyesters was noted with mono-, di- and tri-cyclic anhydrides. However, the measured molecular weights of the polymers were consistently low due to the chain transfer process attributed to trace amounts of water or diacid generated through hydrolysis of the cyclic anhydride. This phenomenon has been widely observed in the copolymerization of epoxides and cyclic
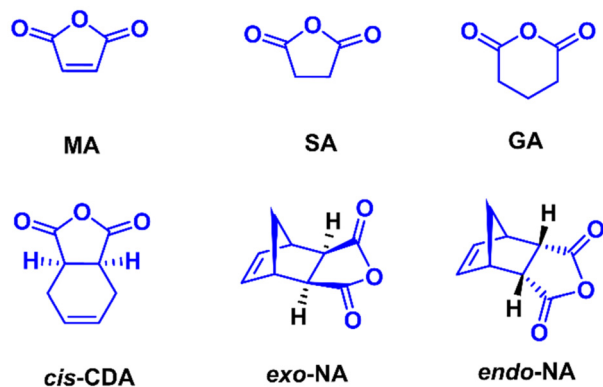
Table 1 Summary of the copolymerization of CFGE with phthalic anhydride[a]

Entry	Cat.	Co-cat	Solvent	T (°C)	t (h)	Conv.[b] (%)	M_n[c] [kg mol^{-1}]	$Đ$[c]
1	1	PPNCl	Toluene	90	1	99	5.87	1.12
2	1	PPNCl	Toluene	70	18	99	5.27	1.15
3	1	PPNCl	PC	90	18	99	4.20	1.25
4	1	PPNCl	PC	120	1	99	4.23	1.32
5	2	PPNTFA	PC	120	1	69	3.32	1.38
6	3	—	PC	120	1	67	4.26	1.77
7	1	—	PC	120	1	70	3.38	1.37
8	—	PPNCl	PC	120	1	21	3.15	1.51

[a] Reactions were performed on the scale of 0.0068 mmol of catalyst, using ratios of 1/1/250/250 for catalyst/cocatalyst/CFGE/PA; solvent (0.5 mL) in a 20 mL glass vial. [b] Determined by relative integration of epoxide *versus* reaction products in the ^1H NMR spectrum (CDCl$_3$, 400 MHz) of the reaction mixture. [c] Determined by gel permeation chromatography (GPC) in THF, calibrated against broad and narrow polystyrene standards.

Fig. 1 Bio-based mono-cyclic, bi-cyclic and tri-cyclic anhydrides utilized in this work.

anhydrides.[21] Notably, under identical reaction conditions, using maleic anhydride as the substrate resulted in the formation of polyesters with significantly higher molecular weights, likely due to extensive cross-linking.[22]

The copolymers were further thoroughly characterized using spectroscopic techniques, including FT-IR, ^1H NMR, and ^{13}C NMR, which strongly supported their formation (see the SI). In the FT-IR spectrum, the characteristic polyester band

was observed at 1730 cm^{-1}. In the ^1H NMR spectrum, the resonance of –CH– protons in the polyester linkage appeared between 5.0 and 5.5 ppm, providing clear evidence for the formation of alternating copolymer structures. Similarly, the ^{13}C NMR spectrum of the copolymer showed a characteristic ester carbon peak at δ = 164–173 ppm, indicating that the copolymer possesses an alternating structure. The thermal properties of all synthesized polyesters were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The copolymers displayed $T_{d5\%}$ in the range of 190 °C for poly(CFGE-*alt*-CHC) to 300 °C for poly(CFGE-*alt*-GA) and glass transition temperatures (T_g) within the range of −12.4 °C for poly(CFGE-*alt*-GA) to 40.1 °C for poly(CFGE-*alt*-exo*-NA) (Table 2). Varying the cyclic anhydride resulted in a T_g increase following the order NA > PA > CDA > MA > SA > GA, indicating that higher monomer rigidity correlates with elevated T_g values.[17a]

The ^1H NMR spectra of polyesters synthesized using CFGE and *exo*-NA or *endo*-NA employing a binary Cr(salen)Cl (1)/ PPNCl catalyst system in propylene carbonate are displayed in Fig. 2. C–H proton signals corresponding to the 1,4-positions and the 2,3-positions of the norbornene ring were shown to appear at 3.04 and 2.58 ppm, respectively. Also, the olefinic protons were observed at 6.17 ppm. This suggests that the ester groups are situated on the same side as the methylene

Polymer Chemistry

Table 2 Summary of the copolymerization of CFGE with cyclic anhydride[a]

Entry	Cyclic anhydride	Cat.	Co-cat	Conv.[b] (%)	M_n[c] [kg mol^{-1}]	$Đ$[c]	$T_{d5\%}$[d] (°C)	T_g[e] (°C)
1	Phthalic (PA)	1	PPNCl	99	4.23	1.32	240	29.3
2	Maleic (MA)	1	PPNCl	78	41.58	1.57	260	16.7
3	Succinic (SA)	1	PPNCl	80	4.90	1.44	280	2.9
4	Glutaric (GA)	1	PPNCl	81	2.02	1.13	300	−12.4
5	Cyclohexene (CDA)	1	PPNCl	77	2.24	1.34	190	21.8
6	*exo*-NA	1	PPNCl	99	5.27	1.64	240	40.1
7	*endo*-NA	1	PPNCl	99	6.60	2.57	230	36.1

[a] Reactions were performed on the scale of 0.0068 mmol of catalyst, using ratios of 1/1/250/250 for catalyst/cocatalyst/CFGE/anhydride; solvent (0.5 mL) in a 20 mL glass vial at 120 °C for 1 h. [b] Determined by relative integration of epoxide *versus* reaction products in the ¹H NMR spectrum (CDCl₃, 400 MHz) of the reaction mixture. [c] Determined by gel permeation chromatography (GPC) in THF, calibrated against broad and narrow polystyrene standards. [d] $T_{d5\%}$ is the degradation temperature corresponding to 5% mass loss of the polymer determined through TGA. [e] The glass transition temperature (T_g) was obtained from the second heating cycle using DSC.
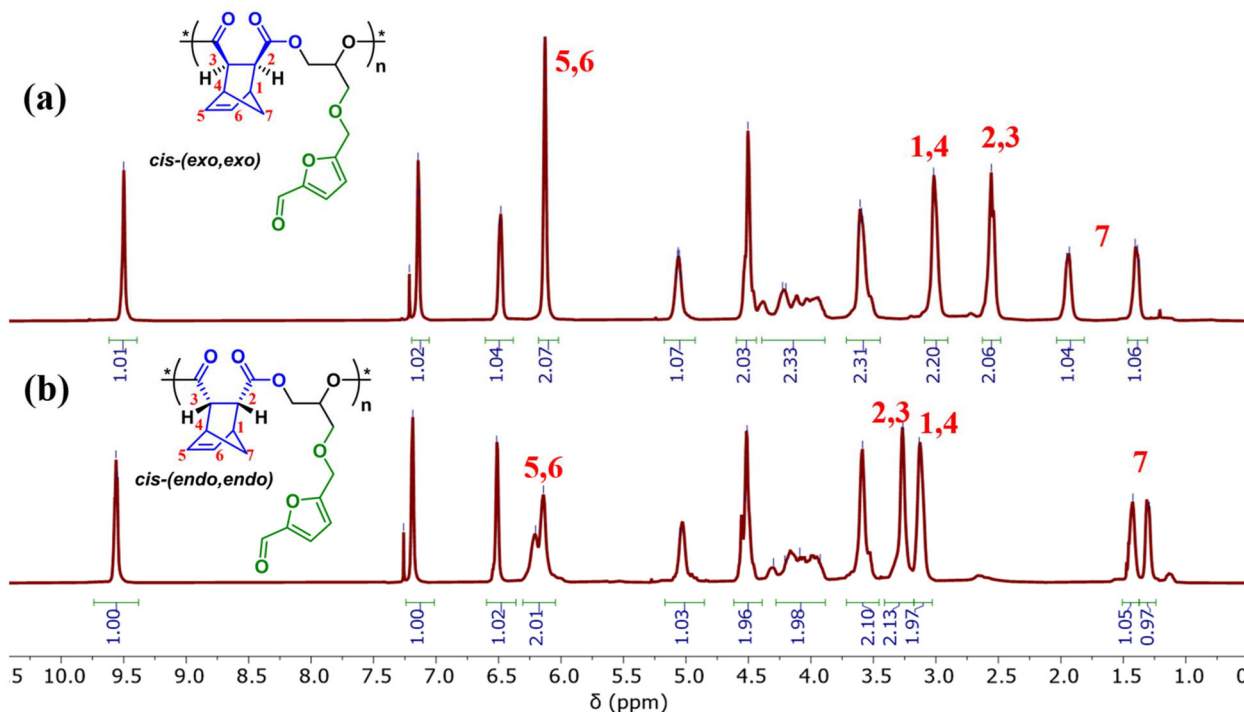

Fig. 2 ¹H NMR spectra of poly(CFGE-*alt*-NA) in CDCl₃. (a) *cis*-(*exo,exo*)polyester produced from *exo*-NA and (b) *cis*-(*endo,endo*)polyester produced from *endo*-NA.

bridge of the norbornene ring as *exo*-NA and confirms that the resulting polyester is composed of *cis*-2,3-(*exo,exo*) ester units. Likewise, the polyester obtained using *endo*-NA retained its original *cis*-2,3-(*endo,endo*) conformation throughout the

copolymerization process without undergoing structural rearrangement.[23a] It is worth noting that this behavior differs markedly when PPNCl is used as the catalyst, where *endo*-NA underwent isomerization and produced *trans*-polyester.[23b] This

analysis was further supported by HSQC and NOESY spectra of the copolymers obtained using *exo*-NA and *endo*-NA with CFGE (Fig. S28–S31).
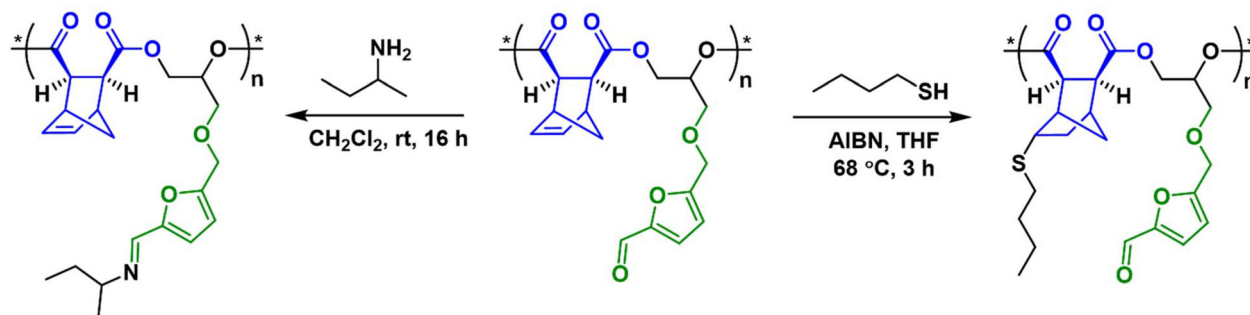
We further investigated functionalization of the pendant aldehyde functionality for post-polymer modification processes. For example, condensation reactions of the poly(CFGE-*alt*-PA) pendant aldehyde using primary amines bearing various functionalities such as alkene (allyl amine), alkoxysilane ((3-aminopropyl)triethoxysilane), and 1,5-diaminopentane were carried out (Scheme S3). The condensation reactions produced the corresponding imines, which have garnered considerable interest in biomedical applications, mainly in drug delivery systems due to the pH-responsive characteristics of imine bonds.[24] These reactions where examined by FT-IR spectroscopy. A carbonyl group (C=O) of an aldehyde peak at 1681 cm^{-1} disappeared and an imine (C=N) peak at 1651 cm^{-1} appeared during the course of the reaction (Fig. S32). In the ^{1}H NMR analysis, an aldehyde –CH– proton signal at 9.56 ppm in the copolymer disappeared, and the corresponding imine peak appeared at 7.97 ppm (allyl amine) (Fig. S33). Diamines resulted in cross-linked materials that were insoluble in common solvents, which limited our characterization to FT-IR spectroscopy (Fig. S34–S36), thus offering an opportunity to incorporate degradable crosslinks that could enhance mechanical properties.[25]

As mentioned earlier, Coates' group demonstrated orthogonal functionalization reactions of aldehyde functionalized polyesters using the VGE epoxy monomer.[8a] This was realized *via* terpolymerization with propylene oxide (PO) and tricyclic anhydride (CPMA), facilitated by a (salph)Al catalyst and a bifunctional cocatalytic system. The resulting poly(PO-*alt*-CPMA, 88%)-*ran*-poly(VGE-*alt*-CPMA, 12%) was subjected to orthogonal post-polymerization modification to enable further functionalization with both alkene and aldehyde groups. Likewise, the polyester obtained from the copolymerization of CFGE and *exo*-NA, having the pendant aldehydes from the CFGE and norbornene featuring a readily functionalizable carbon–carbon double bond, is an ideal candidate and offers a versatile platform for post modification. We first evaluated the post-polymerization modification of poly(CFGE-*alt*-*exo*-NA) by converting the aldehyde into an imine through reaction with *sec*-butylamine (Scheme 2). In a reaction monitored by FT-IR

spectroscopy, the aldehyde (C=O) peak at 1681 cm^{-1} diminished and the corresponding imine (C=N) peak at 1647 cm^{-1} increased during the reaction without affecting the polyester functional infrared peak at 1743 cm^{-1} (Fig. S36). In ^{1}H NMR analysis, the aldehyde –CH– proton signal at 9.56 ppm in the copolymer disappeared and a new signal at 7.97 ppm appeared assigned to the corresponding imine functionality (Fig. 3). GPC analysis of the resultant polyester displayed a slight increase in molecular weight (M_n) from 5.26 to 5.56 kg mol^{-1} (Fig. S41).

Next, we explored the thiol-ene reaction with poly(CFGE-*alt*-(*exo*-NA)), since this type of chemistry has been previously applied to polyesters featuring alkenes from norbornene-type units in their backbone, which were synthesized *via* the copolymerization of epoxides and cyclic anhydrides.[8a,26,27] To investigate the effectiveness of this orthogonal functionalization strategy, a reaction between poly(CFGE-*alt*-(*exo*-NA)) and 1-butanethiol was carried out (Scheme 2). The reaction proceeded selectively to the alkene substituents under AIBN/heat catalyzed conditions resulting in a complete conversion of the alkene group resonance at 6.17 ppm, leading to butyl thioether substitution within 3 h at 60 °C with an increased M_n from 5.26 to 6.63 kg mol^{-1} (Fig. 4 and S41). It is worth noting that over this time the aldehyde functionality, with resonance at 9.56 ppm, remained intact, due to the formation of hemithioacetal/thioacetal between aldehyde and thiol functional groups.[28] This suggests that the orthogonal functionalization strategy can be demonstrated by any sequential combination of imine/thiol-ene reactions.

In order to further support the orthogonality between the two PPM reactions, double post-polymerization modifications were carried out in a one pot. Poly(CFGE-*alt*-(*exo*-NA)) was reacted with *sec*-butylamine and 1-butanethiol in the presence of AIBN at 60 °C for 3 h (Scheme 3). In the IR spectrum, the appearance of the corresponding imine peak and the absence of the aldehyde peak were observed. Similarly, in the ^{1}H NMR of the resultant polymer, the disappearance of both aldehyde and alkene group resonances at 9.56 ppm and 6.17 ppm was observed and the corresponding imine peak appeared at 7.97 ppm (Fig. 5). As expected, the molecular weight (M_n) increased from 5.26 to 8.48 kg mol^{-1} (Fig. S41). These results demonstrate that the two PPM reactions proceed independently and can be applied either sequentially or concurrently to polymers featuring an aldehyde and an alkene from the nor-

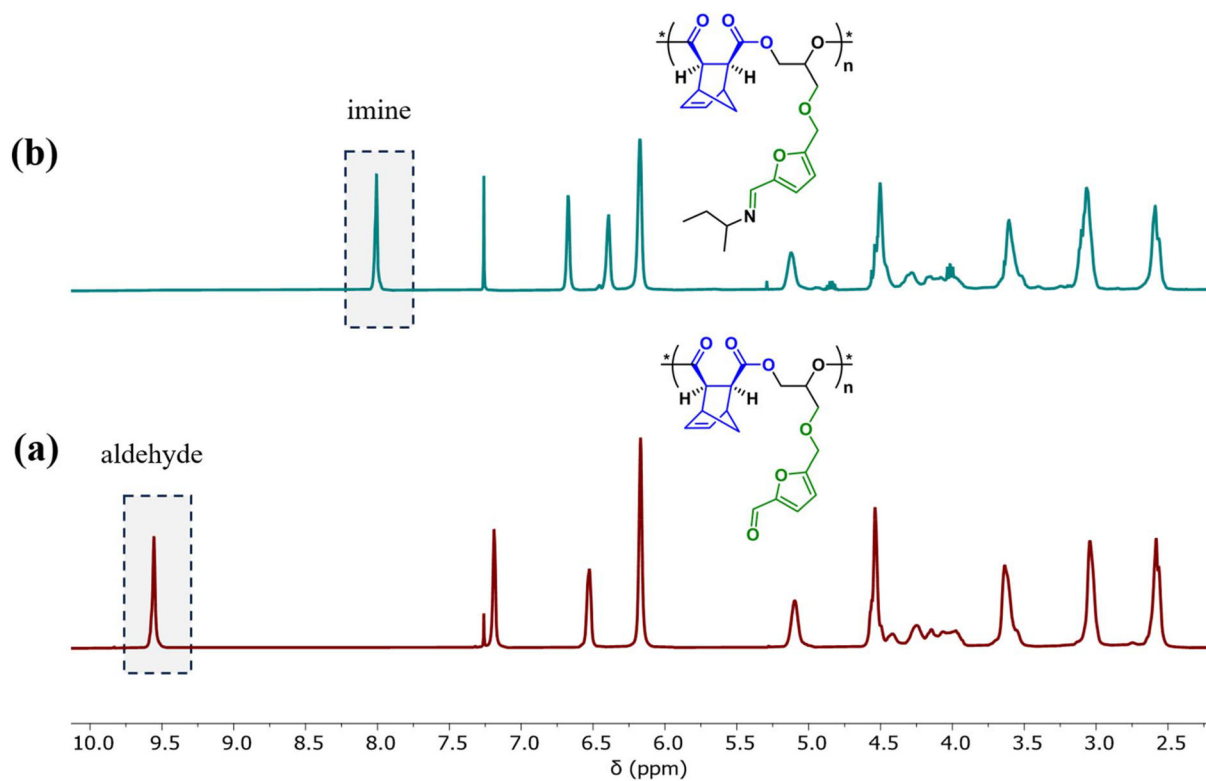**Scheme 2** Post-polymerization modification of poly(CFGE-*alt*-*exo*-NA).

Fig. 3 ^{1}H NMR of poly(CFGE-*alt*-(*exo*-NA)) with *sec*-butylamine (CDCl$_3$, 400 MHz): (a) before and (b) after imine functionalization.
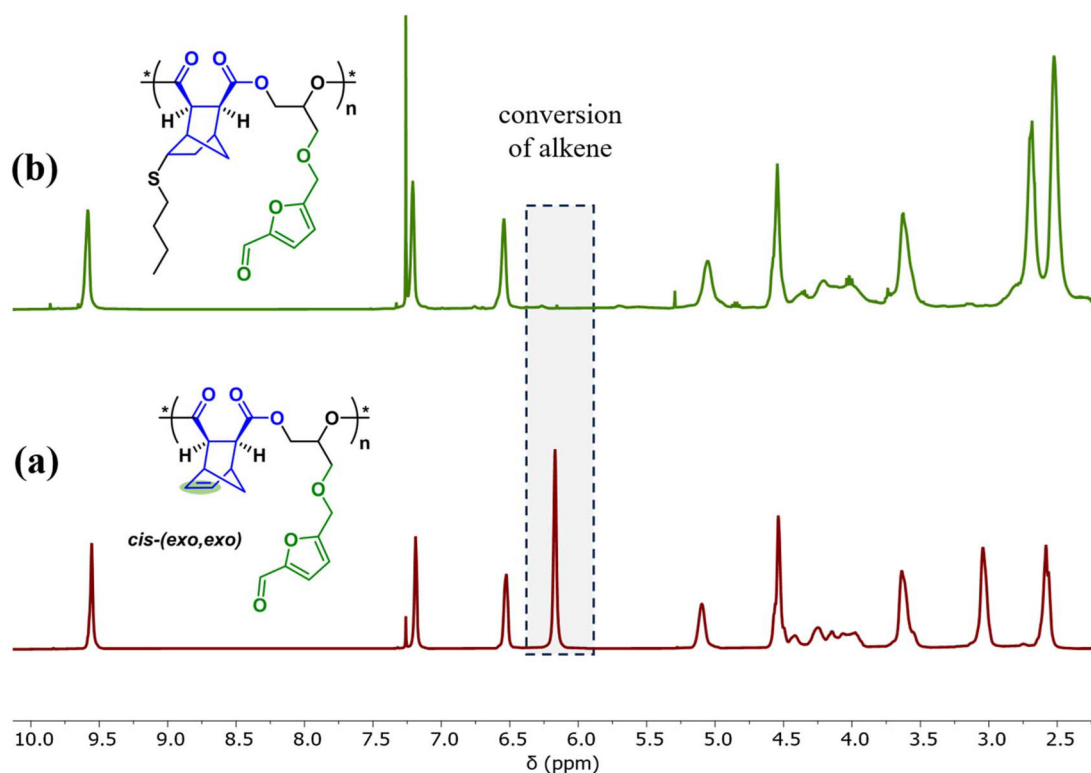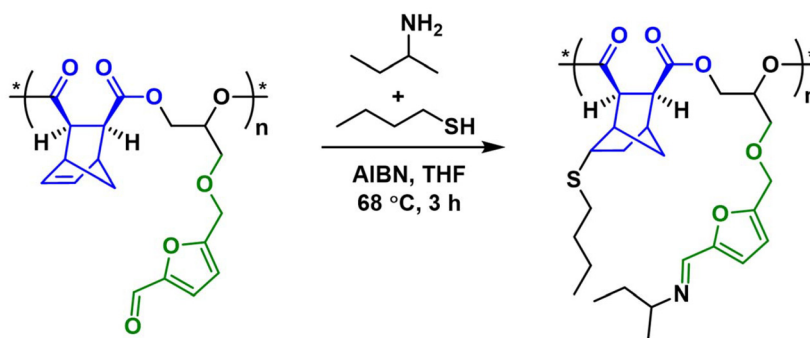

Fig. 4 ^{1}H NMR of poly(CFGE-*alt*-(*exo*-NA)) with 1-butanethiol (CDCl$_3$, 400 MHz): (a) before and (b) after thiol-ene functionalization.

Scheme 3 One pot double PPM of poly(CFGE-*alt*-(*exo*-NA)) with amine and thiol.
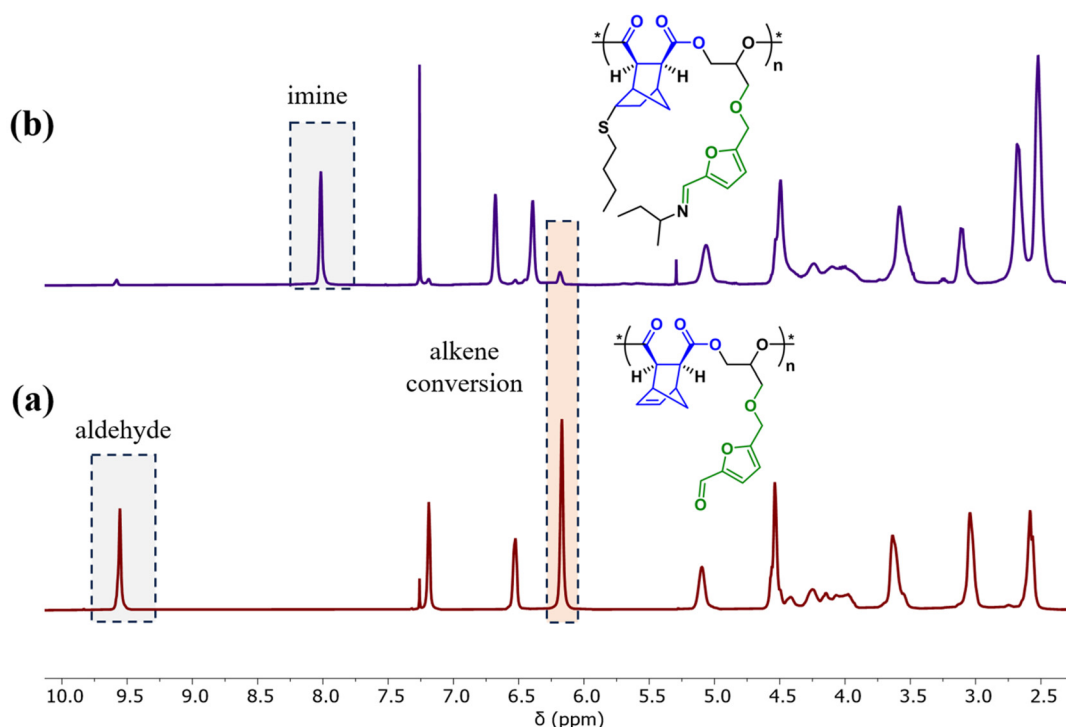

Fig. 5 ¹H NMR of one pot double PPM of poly(CFGE-*alt*-(*exo*-NA)) with amine and thiol (CDCl₃, 400 MHz): (a) before and (b) after double functionalization.

bornene-type backbone. Another interesting reactivity was observed with the use of cysteamine in which both amine and thiols reacted with the poly(CFGE-*alt*-(*exo*-NA)) aldehyde group resulting in the corresponding thiazolidine derivative polymer (Scheme S6). For a comprehensive discussion of the specific performance and potential applications of post-polymerization modified polymers, see ref. 29.

Conclusion

In summary, we have described a biobased HMF derived epoxy monomer for the direct production of aldehyde-functionalized polyesters when coupled with cyclic anhydrides. The copoly-

merization process was carried out in the presence of a binary Cr(salen)Cl (**1**)/PPNCl catalyst system using propylene carbonate as a solvent. The process demonstrated the utilization of a renewable epoxy monomer and cyclic anhydrides, and the use of propylene carbonate as a solvent, making the reaction more sustainable. The presence of aldehyde functional groups on the polyesters provided a site for post-polymerization functionalization reactions with primary amines. Also, we successfully demonstrated an orthogonal post-polymerization modification (PPM) behavior relative to the aldehyde and alkenes present in poly(CFGE-*alt*-(*exo*-NA)). Both the aldehyde-to-imine and thiol-ene PPM reactions proceeded selectively and independently, enabling a one-pot double PPM strategy. We believe that this strategy offers a sustainable route to

synthesizing customizable aliphatic polyesters with broad application potential.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: https://doi.org/10.1039/d5py00800j.

Acknowledgements

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