Catalytic Ring-Opening Copolymerization of Fatty Acid Epoxides: Access to Functional Biopolyesters

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ABSTRACT: Fatty acid epoxies serve as valuable starting materials for the development of bio-based polyesters. Here we present a new and efficient catalytic process that allows for the copolymerization of fatty acid-based epoxides and various cyclic anhydrides under attractive process conditions affording functional polyesters. The degree of functionalization and the nature of the polymer backbone can be modulated via monomer design. Postpolymerization cross-linking processes were examined to create rigid macromolecular networks that build on orthogonal polyester functionality, creating possible entries for materials with switchable thermal and mechanical properties.

- range of functional polyesters
- valorization of fatty acid waste
- reversible cross-linked materials
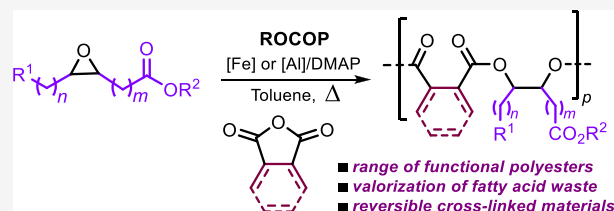
INTRODUCTION

Driven by a current and future need for chemical circularity,[1−3] our society aims at developing solutions for issues related to global plastic disposal and recycling[4] and the potential risk of accumulating microplastics in our ecosystems.[5] Ideally, polymers derived from renewable monomers[6−8] are designed to address this sustainability challenge, while considering important aspects such as recyclability, raw material accessibility, and cost. There is therefore a huge focus on the development of new (catalytic) processes that enable precision synthesis of well-defined smaller and larger functional bio-based macromolecules.[9,10]

Among the readily available renewable biocompounds, both terpenes[11,12] and long-chain "fatty" acids[13,14] have conquered a prominent position as versatile monomers in polymer science. The wide structural diversity of terpenes makes them ideal candidates to explore structure−property relationships enabled by postsynthetic modifications and in particular when focusing on polyesters[15−18] or polycarbonates[19−23] as the macromolecular targets. Both types of polymers are widely studied for different reasons. While aliphatic polyesters possess potential toward biodegradation,[24] the search for new polycarbonates has received impetus from the increasing concerns surrounding toxic metabolites of commercial polycarbonate that is based on bisphenol A.[25]

Between the known polymerization routes to polyesters, step-growth approaches[26,27] and ring-opening polymerization (ROP) of lactones[18] have reached maturity, but undoubtedly the most efficient way to produce polyesters while conceiving new, more functional and tunable architectures is represented by ring-opening copolymerization (ROCOP)[28] of epoxides and cyclic anhydrides.[29] Catalytic ROCOP processes have been developed by various groups over the years (Scheme 1a),[15,16,30−33] though less progress has been noted with sterically challenging combinations of both types of monomers

(Scheme 1b).[34−36] Therefore, there is a key role for detailed mechanistic understanding[37] to guide catalyst evolution in this area toward the efficient transformation of bulky monomers allowing biomass-related feedstock to become feasible precursors in polyester synthesis.

Metal−salen-based binary catalysts have long dominated the ROCOP of epoxides and cyclic anhydrides.[38] Our group has developed powerful binary catalysts that consist of a metal aminotriphenolate complex (M = Al, Fe) and a halide salt. These aminotriphenolate complexes combine the requisite Lewis acidity with a conformationally flexional ligand backbone that together allow for effective activation of sterically congested epoxides.[39−41] More recently, we showed that both Fe- and Al-based binary catalysts are also useful in the context of aliphatic polyester synthesis using terpene oxides as monomers.[15,34,35] Therefore, we wondered whether our binary systems would be useful toward the creation of functional polyesters by coupling of fatty acid epoxides and cyclic anhydrides. The catalytic ROCOP of such a monomer combination remains underdeveloped (Scheme 1b),[42,43] and a successful development could thus create new incentives for industrial waste streams that have a significant content of (unsaturated) fatty acid components. Relevant to this work is also the recent copolymerization of cyclic anhydrides and disubstituted epoxides with both *trans*- and *cis*-structures reported by Lu and co-workers,[44,45] with significant lower reactivity observed for the *trans*-configured epoxides.
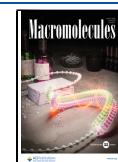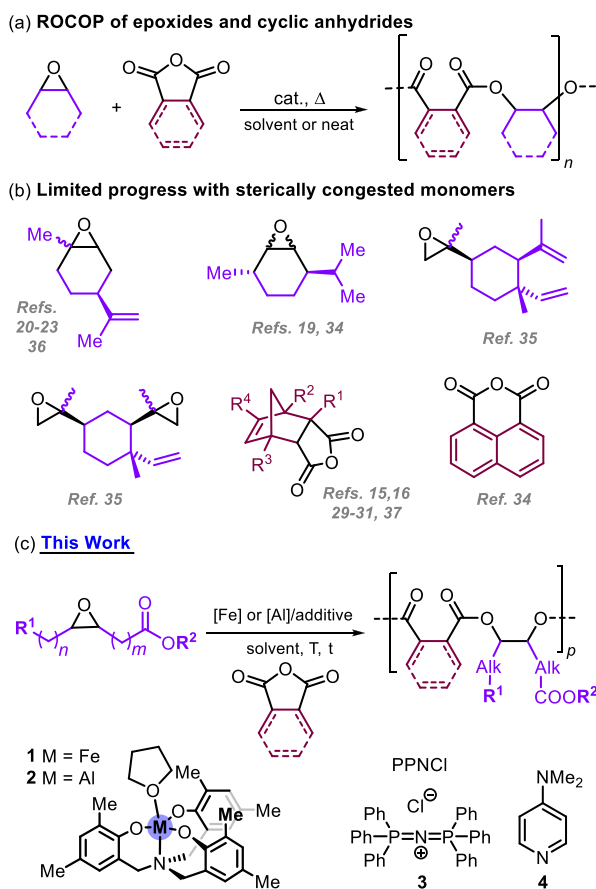
Scheme 1. Catalytic ROCOP of Epoxides and Cyclic Anhydrides (a), Limited Progress with Bulky Monomers (b), and This Work (c)

(a) **ROCOP of epoxides and cyclic anhydrides**

(b) **Limited progress with sterically congested monomers**

(c) **This Work**

Table 1. ROCOP of Phthalic Anhydride (PA) and Methyl Oleate Oxide (MOO) Catalyzed by Binary Catalysts Derived from 1 or 2 and Initiators 3 or 4[a]

entry	cat.	solv	T, t (°C, h)	conv[b] (%)	M_n/Đ[c]
1	1+3	THF	60, 6	<1	n.d.
2	1+3	Tol	60, 6	5	n.d.
3	1+3	Tol	110, 6	84	6.3, 1.21
4	1+3	neat	110, 6	97	8.1, 1.24
5	1+3	Tol	110, 6	14	4.1, 1.16
6	2+3	Tol	110, 6	53	4.1, 1.17
7	1+4	Tol	110, 6	61	5.1, 1.33
8	2+4	Tol	110, 6	25	4.3, 1.15
9	1+3	Tol	110, 16	98	6.8, 1.21
10	1+4	Tol	110, 24	87	5.2, 1.21
11	2+3	Tol	110, 24	>99	8.9, 1.25
12	2+4	Tol	110, 24	>99	11.2, 1.24
13	2+4	neat	110, 24	98	9.98, 1.35
14[d]	2+4	Tol	110, 24	90	8.7, 1.29
15[e]	2+4	Tol	110, 24	>99	4.7, 1.22
16[f]	2+4	Tol	110, 24	>99	1.8, 1.16
17[g]	2+4	Tol	110, 24	>99	12.0/1.19

[a]Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), initiator and [M] (both 1 mol %), solvent (0.25 mL, 3.0 M), MOO/[M] = 100 except for entry 5:200. [b]Determined by ¹H NMR analysis. [c]Determined by GPC in THF calibrated with polystyrene standards, M_n values are given in kg/mol. [d]In the presence of 0.01 equiv of BnOH. [e]In the presence of 0.05 equiv of BnOH. [f]MOO prepared from industrial duck fat containing about 80% oleate. [g]As for footnote f, but by using purified MOO. n.d. stands for not determined.

Here we report a new catalytic ROCOP process that gives clean access to fatty acid-derived polyesters (Scheme 1c). The structural features of these polyesters were varied by diversifying the nature of both monomers and the acid protecting groups. Furthermore, the catalytic ROCOP process was also feasible by using a waste-stream-based sample of oleic acid as a precursor. Lastly, terminal-alkyne and furan-functionalized polyesters were probed as irreversible and thermoreversible cross-linked materials.

■ RESULTS AND DISCUSSION

On the basis of our previous work,[15,20,34,35] we started our screening with Fe and Al complexes **1** and **2** and initiators bis(triphenylphosphine)iminium chloride (PPNCl, **3**) and 4-(dimethylamino)pyridine (DMAP, **4**). As a representative fatty acid, we selected oleic acid, which was first protected and epoxidized to deliver the substrate methyl oleate oxide (MOO, Table 1), while phthalic anhydride (PA) was utilized as a benchmark comonomer. A wide screening of reaction conditions was performed (see Tables S1 and S2 in the Supporting Information for an additional list of results), and selected experiments are reported in Table 1. All experiments were conducted by using a slight excess of PA as it can be easily removed in the polymer purification step.

Initial trails were performed by using complex **1** in the presence of PPNCl (**3**) in THF and toluene as solvent (Table 1, entries 1−3). At 60 °C, only traces of product were observed; therefore, we probed a higher reaction temperature

(entry 3, 110 °C), and this change was beneficial toward polymer formation (84%) and the target poly(MOO-*alt*-PA) had an M_n of 6.3 kg/mol with a narrow dispersion (Đ) of 1.21. The reaction in the absence of solvent (entry 4) provided the polyester with an improved M_n of 8.1 kg/mol while retaining a low Đ of 1.24. The influence of a lower catalyst loading (entry 5, MOO/**1** = 200) was also examined, giving much lower conversion of the epoxide monomer (14%). Other binary catalysts were then considered (entries 6−8) by using both Fe-complex **1** and Al-complex **2**, with either PPNCl **3** or DMAP **4** at 110 °C. While all catalysts were active toward the formation of poly(MOO-*alt*-PA), the best results are reported in entry 4. Because incomplete MOO conversion was noted, the reaction times were extended to 16 h (entry 9) and 24 h (entries 10−13). The highest molecular weight (11.2 kg/mol) was attained with Al-complex **2** in the presence of DMAP with complete conversion of MOO (entry 12). Though comparable MOO conversion was reached in the absence of a solvent (entry 13), the M_n and Đ were slightly lower and higher, respectively.
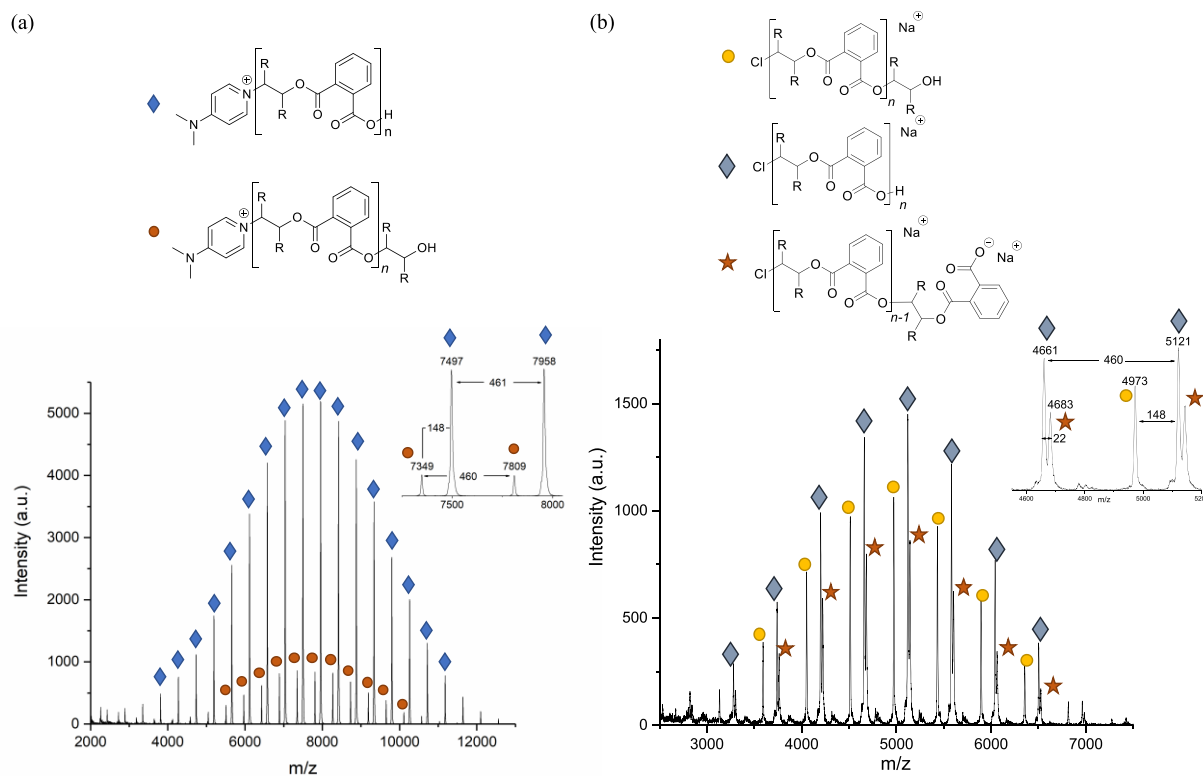
Figure 1. MALDI-ToF spectra of poly(MOO-*alt*-PA) obtained with **2**/DMAP (a, entry 12, Table 1) or **1**/PPNCl as catalyst (b, entry 9, Table 1).

The formation of this polyester was first confirmed by NMR analysis, showing that the ROCOP of epoxides and anhydrides takes place in a controlled manner leading to the selective formation of poly(MOO-*alt*-PA) while no ether linkages could be detected. The resulting polymers showed monomodal and quite narrow molecular weight distributions ($Đ = 1.17-1.24$) as measured by GPC when **2**/DMAP was used as catalyst and bimodal ones when Fe-complex **1** was present (see the Supporting Information, section on GPC). Bimodal distributions generated by complex **1** in other types of ROCOP processes have been observed previously and discussed in detail.[15] The obtained polymers were further characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF).

In the MALDI-ToF spectra of selected samples (entries 9 and 12, Table 1, and Figure 1), no cyclic polymers were detected while different distributions could be identified and assigned. When a combination of Al-complex **2** and DMAP was used as a binary catalyst, the MALDI-ToF analysis (Figure 1a) showed two major DMAP-initiated polymer species with distributions having peak separations of around 460 mass units. The major pattern (blue diamonds) corresponds to a polymer having a COOH end-group, whereas the minor pattern (red dot) could be ascribed to polyester molecules containing a molecule of ring-opened, protonated MOO as end-group.

The polyester produced by Fe-complex **1** in the presence of PPNCl **3** as initiator (Figure 1b) showed the presence of three distributions in the MALDI spectrum which all correspond to Cl-initiated polymer species. The major distribution (gray diamonds) relates to polyesters with a COOH end-group and an associated Na cation, while a second distribution (orange stars) is 22 mass units upshifted and was tentatively assigned to polyesters with a deprotonated carboxylate end-group and two

complexed Na cations. The third pattern (yellow dots) matches the predicted values for polyesters with a ring-opened, protonated MOO terminus.

To gain further insight into the polymerization process catalyzed by binary catalysts **1**/PPNCl, **1**/DMAP, **2**/PPNCl, and **2**/DMAP, these ROCOP processes performed in toluene at 110 °C leading to poly(MOO-*alt*-PA) were followed in time. In all cases, a set of parallel experiments were conducted allowing to analyze (without perturbing the reaction mixture) their composition by ^{1}H NMR and GPC to determine the conversion of MOO, the selectivity of the process, and the M_n and $Đ$ values of poly(MOO-*alt*-PA); see the Supporting Information for full details (Figures S3−S6).

The binary catalyst comprised of Fe-complex **1** and PPNCl promotes the copolymerization of MOO and PA in a shorter reaction time (Table 1; entry 3 vs 8). Therefore, we monitored the polymerization process over a longer period of time (>6 h) and found that the M_n (5.1 kg/mol) and $Đ$ (1.24) do not further change after ∼70% MOO conversion (see Figure S3). The Al-containing binary system **2**/PPNCl provided a gradual and nearly linear conversion profile for MOO while the M_n steadily increased (Figure S5). The copolymerization process in the presence of Al-complex **2** and DMAP shows the highest degree of control giving comparatively longer polymeric chains (Figure 2 and Figure S6) compared to the other binary catalysts. The increase in M_n in this latter case is pseudo-linear with increasing MOO conversion, and apparently there is a higher tendency for the more Lewis acidic Al-complex to retain the growing polymer chain within its coordination sphere. Both the nature of the Lewis acid and the potential of the initiator are important to reach optimal reactivity, selectivity, and polymer quality in these ROCOP processes.
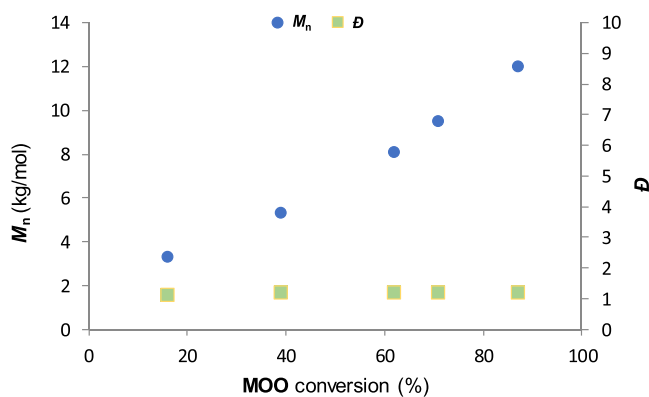
**Figure 2.** Copolymerization of MOO and PA mediated by **2**/DMAP over time.

As generally observed with many ROCOP catalysts, the number-average molecular weight values M_n for the poly-(MOO-*alt*-PA) samples obtained are lower than the theoretical ones for a living system. This is often attributed to the presence of traces of protic impurities such as acid (from the hydrolysis of PA) and/or water that can act as chain transfer agents without affecting the activity of the catalytic system. At this point, we examined the possibility to control the molecular weight of the polyester by a chain transfer agent (CTA) added during the ROCOP of MOO and PA and selected the binary couple **2**/DMAP that gave the highest M_n and low Đ (Table 1, entry 12) with a monomodal distribution. The use of an alcohol as a CTA in the ROP of cyclic esters offers the advantage of optimizing the productivity and minimizing the contamination of polymer with metal residues.[46]

End-group analysis of poly(MOO-*alt*-PA) produced in the presence of BnOH by ^{1}H NMR spectroscopy clearly showed that the polymer chains were end-capped with a benzyl−oxy group (see Figure S7). We investigated the role of BnOH as a CTA by using different amounts (0.01 and 0.05 equiv; see Table 1, entries 14 and 15) observing, as expected, that a higher amount of BnOH provided the polyester with a reduced molecular weight without changing the dispersity (Figures S8 and S9).

With the optimal conditions determined for binary catalyst **2**/DMAP (entry 12, Table 1), we wondered whether an industrial food waste sample of oleic acid (duck fat, provided by Sapoval, France) could be used as a feedstock to produce poly(MOO-*alt*-PA). The duck fat waste stream contains up to around 80% of sodium oleate that was first converted on multigram scale to MOO, then treated with CaH_2 to remove traces of H_2O, and used as such as a monomer without further purification. As expected, the use of this lower-grade MOO led only to oligo(MOO-*alt*-PA) with an M_n of 1.8 kg/mol probably as a result of impurities acting as CTAs (Table 1, entry 16). However, when properly purified by column chromatography (entry 17), poly(MOO-*alt*-PA) with nearly identical properties to those reported in entry 12 was obtained.

We decided to extend the copolymerization to other bio-based cyclic anhydrides (Table 2, succinic anhydride, SA, and maleic anhydride, MA; entries 2 and 3). The formation of poly(MOO-*alt*-SA) and poly(MOO-*alt*-MA) proceeds selectively though significantly slower with incomplete epoxide conversion compared to the ROCOP of MOO and PA (entry 1). Both SA and MA are known to be more sluggish monomers in the formation of polyesters through ROCOP methods.[29]

Table 2. ROCOP of MOO and Other Fatty Acid Epoxides with Cyclic Anhydrides Promoted by 1/PPNCl or 2/DMAP as Binary Catalyst[a]
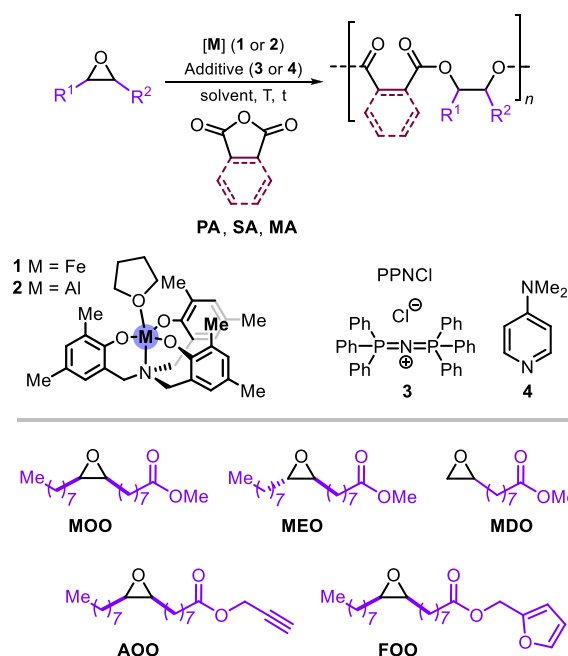
entry	cat.	monomers	t (h)	yield[b] (%)	$M_n/Đ$[c]
1	**2/4**	MOO/PA	24	80	11.2/1.24
2	**2/4**	MOO/SA	48	50	4.4/1.16
3	**2/4**	MOO/MA	48	40	5.1/1.66
4	**2/4**	MEO/PA	48	60	6.0/1.22
5	**2/4**	MDO/PA	3	85	15.9/1.20
6	**2/4**	AOO/PA	24	82	9.4/1.49
7[d]	**2/4**	AOO/PA	24	75	10.9/1.50
8	**2/4**	FOO/PA	24	78	7.0/1.41
9[d]	**2/4**	FOO/PA	24	84	6.8/1.61
10	**1/3**	MDO/PA	1.5	84	6.5/1.27
11	**1/3**	MEO/PA	24	80	3.2/1.16
12	**1/3**	AOO/PA	9	83	5.8/1.41
13	**1/3**	FOO/PA	9	85	6.8/1.35

[a]Reaction conditions: MOO (0.75 mmol, 1.0 equiv), PA (0.825 mmol, 1.1 equiv), initiator and [M] (both 1 mol %), toluene (0.25 mL, 3.0 M), MOO/[M] = 100, 110 °C, 9−48 h. [b]Yield of the isolated polymer product after precipitation. [c]Determined by GPC in THF calibrated with polystyrene standards, M_n values in kg/mol. [d]AOO or FOO (3.0 mmol, 1.0 equiv), PA (3.3 mmol, 1.1 equiv), toluene (1.0 mL, 3.0 M).

Nonetheless, the binary system **2/4** (Al-complex and DMAP) proved to be also applicable to these less reactive cyclic anhydrides. Next, we also examined some other fatty acid epoxides (Table 2) to extent the scope/diversity of these polyesters. First, the sterically more congested *trans*-epoxide monomer MEO (i.e., the epoxide derived from the methyl ester of elaidic acid) was subjected to the optimized ROCOP conditions. The coupling of MEO (compared to MOO) with PA was significantly slower (incomplete epoxide conversion) and produced the desired poly(MEO-*alt*-PA) with high selectivity, a modest M_n (6.0), and low Đ (1.22).

The lower reactivity of *trans*-configured epoxides was recently also observed in the catalytic formation of cyclic carbonates.[47] Despite the more challenging nature of the ROCOP of MEO and PA, the Al-based catalyst **2**/DMAP

shows potential for other types of bulky monomers. When the steric impediment around the oxirane was reduced by using a terminal fatty acid epoxide derived from caproleic acid (MDO), the corresponding polyester poly(MDO-*alt*-PA) was prepared in only 3 h and having an M_n of 15.9 kg/mol ($Đ$ = 1.20; Table 2, entry 5). This latter result aligns well with the predicted epoxide monomer reactivity order MDO > MOO > MEO.

To access functional polyesters, the alkyne- and furyl-based epoxy monomers AOO and FOO were prepared (for details see the Supporting Information) by using 2/DMAP as binary catalyst (Table 2, entries 6−9). These functional monomers exhibited similar reactivity as MOO and provided poly(AOO-*alt*-PA) and poly(FOO-*alt*-PA) with a number-average molecular weight of up to 10.9 kg/mol. The synthesis of these functional polyesters could be scaled up three times (i.e., at gram scale) with similar results (entry 6 vs 7 and entry 8 vs 9) and thus allows to modify these polyesters by postsynthetic manipulation (*vide infra*).

Finally, copolymerizations of MEO, MDO, AOO, and FOO with PA were also conducted with the Fe-based binary system 1/PPNCl (entries 10−13), resulting, despite the kinetically more competent nature of these processes, in substantially lower M_n values for the polyesters (except for FOO, entry 13). It should be noted that for all internal epoxides no regioselective ring-opening by neither of the catalyst compositions is expected as the two alkyl chain substituents on the oxiranes have rather similar electronic and steric features.

The thermal properties (glass transition, T_g, and decomposition temperatures, T_d^5) of the obtained polyesters were analyzed (Table 3; see the Supporting Information for further

Table 3. TGA and DSC Analysis of the Polyesters

entry	polyester	$M_n/Đ$[a]	T_g[b] (°C)	$T_d^{5\,c}$ (°C)
1	MOO/PA	11.2/1.24	−20	265
2	MOO/SA	4.4/1.16	−45	312
3	MOO/MA	5.1/1.66	−27	280
4	MDO/PA	15.9/1.20	−5	334
5	MEO/PA	6.0/1.22	−20	289
6	AOO/PA	10.9/1.50	−22	304
7	FOO/PA	6.8/1.61	−19	269

[a]Data taken from Tables 1 and 2. [b]Determined by DSC analysis at a 10 °C/min heating/cooling rate; data are from the second heating cycle. [c]From thermogravimetric analysis; data refer to the values at 5 wt % loss.

details) by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All polyesters have a relatively low T_g, which is likely dominated by the flexible alkyl side chains in these kinds of polymers. A slightly higher T_g (−5 °C) is noted for poly(MDO-*alt*-PA) in line with the lower content of alkyl chains in this polyester. The decomposition temperatures T_d^5 vary from 265 to 334 °C, and differences may be ascribed to both the variances in the polymer backbone and molecular weights. Importantly, the observed high thermal decomposition stability is of value when high-temperature transformations are pursued (*vide infra*).

Both the alkyne- and furan-derived polyesters poly(AOO-*alt*-PA) and poly(FOO-*alt*-PA) were used to explore the preparation of cross-linked materials (Scheme 2). We first screened the Cu(I)-catalyzed azide−alkyne cycloaddition

Scheme 2. Synthesis of Cross-Linked Polyesters from Alkyne- and Furan-Based Precursors[a]
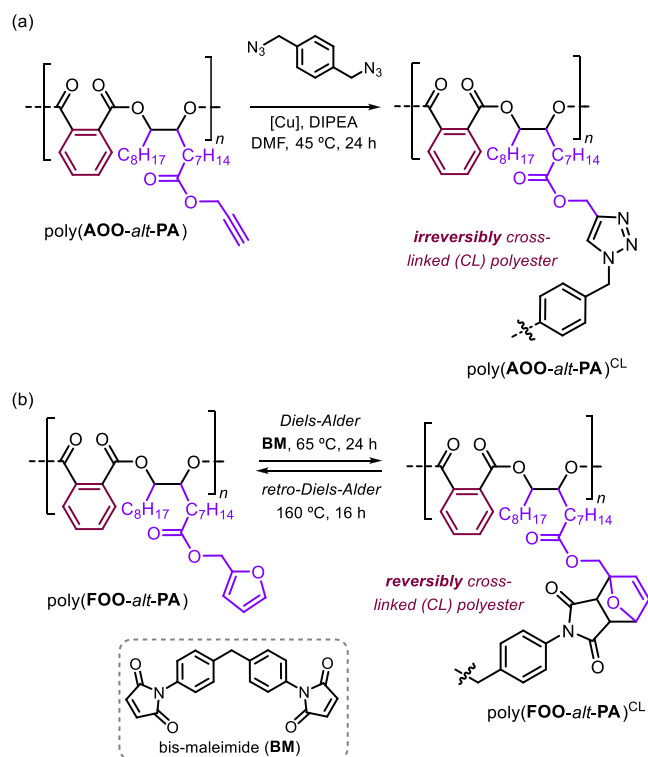
[a]Full reaction conditions: (a) poly(AOO-*alt*-PA) (150 mg), 1,4-bis(azidomethyl)benzene (15 or 50 mol %), CuI (0.10 mol %), DIPEA (5 equiv), DMF (0.1 M), 45 °C, 24 h. (b) Poly(FOO-*alt*-PA) (150 mg), BM (15 or 50 mol %), DMF, 65 °C, 24 (Diels−Alder) or 160 °C, 16 h (*retro*-Diels−Alder).

(CuAAC) reaction (Scheme 2a) by treating poly(AOO-*alt*-PA) with different amounts (15 and 50 mol %) of 1,4-bis(azidomethyl)benzene as cross-linking agent.[48,49] The CuAAC reaction is often orthogonal to other chemistries that are used to modify polymers, and 1,2,3-triazole-bridged products are typically highly stable toward heat, oxidation, and hydrolysis. Two formulations were prepared to access an incomplete and complete cross-linked (CL) poly(AOO-*alt*-PA)[CL].

The resultant polyesters were completely insoluble in DCM and DMSO, supportive of the formation of cross-linked polymer networks. The cross-linking process was followed by FT-IR (see Figures S57−S60) and showed the partial (at 15 mol % of bis-azide) and full (at 50 mol % of bis-azide) disappearance of the terminal alkyne absorption at 3274 cm^{-1} in the parent poly(AOO-*alt*-PA).

Unlike the irreversible cross-linking through CuAAC reactions, the presence of furan groups in the side-chains of the polyester poly(FOO-*alt*-PA) offers synthetic handles for thermally reversible cross-linking by using Diels−Alder (DA) chemistry.[50−54] Therefore, poly(FOO-*alt*-PA) was reacted with the bis-maleimide (BM, Scheme 2b) by using the same amounts (15 and 50 mol %) of cross-linking agent as used in the CuAAC reactions. The resulting polymers, poly(FOO-*alt*-PA)[CL], were also completely insoluble in DCM or DMSO, indicating the formation of cross-linked polymer networks.[55−57] Further evidence was gathered by performing FT-IR analysis, showing spectral features consistent with DA

adduct formation.[55] Before cross-linking, the FT-IR spectrum of the poly(FOO-*alt*-PA)/BM mixture displayed signals of free furan (at 739 and 1503 cm^{-1}) and maleimide rings (at 695 and 826 cm^{-1}), whereas after gel formation, the FT-IR spectrum of poly(FOO-*alt*-PA)^{CL} revealed the virtual complete disappearance of these aforementioned peaks (see the Supporting Information).

The thermally reversible DA process allows to monitor the stability of the cross-linked materials by DSC.[58] As the retro-DA reaction is an endothermic process, disruption of the [4 + 2] cycloadducts can be easily observed between 100 and 150 °C. The DSC analysis for poly(FOO-*alt*-PA)^{CL} revealed two distinct endothermic transitions that relate to the breaking of both *endo-* and *exo-*DA adducts around 110 and 135 °C (see the Supporting Information). The T_g of the fully cross-linked poly(FOO-*alt*-PA)^{CL} was recorded by using a single heating cycle from −80 to 175 °C to avoid any significant degradation due to the occurrence of a retro-DA process. Comparison between the parent poly(FOO-*alt*-PA) and the cross-linked poly(FOO-*alt*-PA)^{CL} provided a $\Delta(T_g)$ of about 95 °C, which further confirms the cross-linked nature of the latter.

The assumed thermoreversibility of the Diels−Alder adducts in poly(FOO-*alt*-PA)^{CL} was then experimentally studied by heating the partially and fully cross-linked polymer in DMF at two different temperatures (Table 4) and the M_n and Đ values

Table 4. Thermoreversible Diels−Alder Reactions of Poly(FOO-*alt*-PA)^{CL} [a]

entry	polyester	T, t (° C, h)	$M_n/Đ$[b]
1	poly(FOO-*alt*-PA)		6.8/1.61[c]
2[d]	poly(FOO-*alt*-PA)^{CL}	120, 5	e
3[f]	poly(FOO-*alt*-PA)^{CL}	120, 5	e
4[d]	poly(FOO-*alt*-PA)^{CL}	160, 16	6.6/1.40
5[f]	poly(FOO-*alt*-PA)^{CL}	160, 16	6.0/1.43

[a]Reaction conditions: poly(FOO-*alt*-PA)^{CL} (150 mg), DMF (40 wt %). [b]Determined by GPC in THF calibrated with polystyrene standards; M_n values in kg/mol. [c]Data from entry 9, Table 2. [d]Partially cross-linked with 15 mol % of BM. [e]No observable conversion of the cross-linked polyester noted. [f]Fully cross-linked with 50 mol % of BM.

of the polymer products were compared to the parent poly(FOO-*alt*-PA) of entry 1. At 120 °C, no observable retro-DA could be noted (entries 2 and 3), and therefore we decided to increase the reaction temperature to 160 °C (entries 4 and 5). Under these latter conditions, the initial heterogeneous mixture became fully homogeneous over time, indicating dissolution of the polymer. Analysis of the products by GPC (Figures S48 and S49) showed that the original poly(FOO-*alt*-PA) had been regenerated with rather similar M_n and Đ. These observations are in line with a fully reversible nature of the cross-linking process.

CONCLUSION

In summary, we have developed a catalytic and well-defined process for the ROCOP of fatty acid epoxides and cyclic anhydrides that allows to create functionalized polyesters. Both the epoxy and the anhydride monomer can be varied providing low-T_g macromolecules with postpolymerization potential toward cross-linked materials. Two of such approaches build on the reactivity of alkynes and furans in cross-linking phenomena, thereby creating both reversibly (Diels−Alder)

and irreversibly (CuAAC) cured compounds. Notably, industry-based, waste oleic acid was also prone to oligo/polyester formation, giving incentives for the valorization of various waste streams that contain (unsaturated) fatty acids. Multiply unsaturated fatty acids may be of great use to design novel polyester architectures with orthogonal functional groups expanding the possibilities of these macromolecules in various areas of polymer science. Our focus will be on bridging our current knowledge toward the design of multifunctional, modular, and bio-based resin and coating materials.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.2c00321.

Analytical data for all polymer samples including TGA, DSC, GPC, NMR, IR, and MALDI spectra; further experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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