

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

Arianna Brandolese, Francesco Della Monica, Miquel À. Pericàs, and Arjan W. Kleij*



Cite This: *Macromolecules* 2022, 55, 2566–2573



Read Online

ACCESS |



Metrics & More

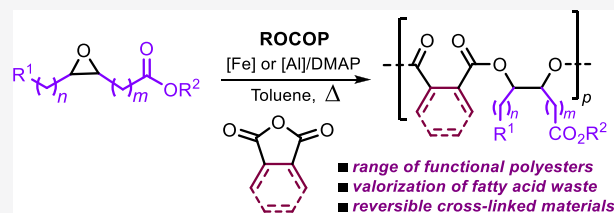


Article Recommendations



Supporting Information

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.



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 recycling⁴ 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 lactones¹⁸ 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

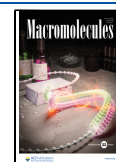
(Scheme 1b).^{34–36} Therefore, there is a key role for detailed mechanistic understanding³⁷ to guide catalyst evolution in this area toward the efficient transformation of bulky monomers allowing biomass-related feedstock to become feasible precursors in polyester synthesis.

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.

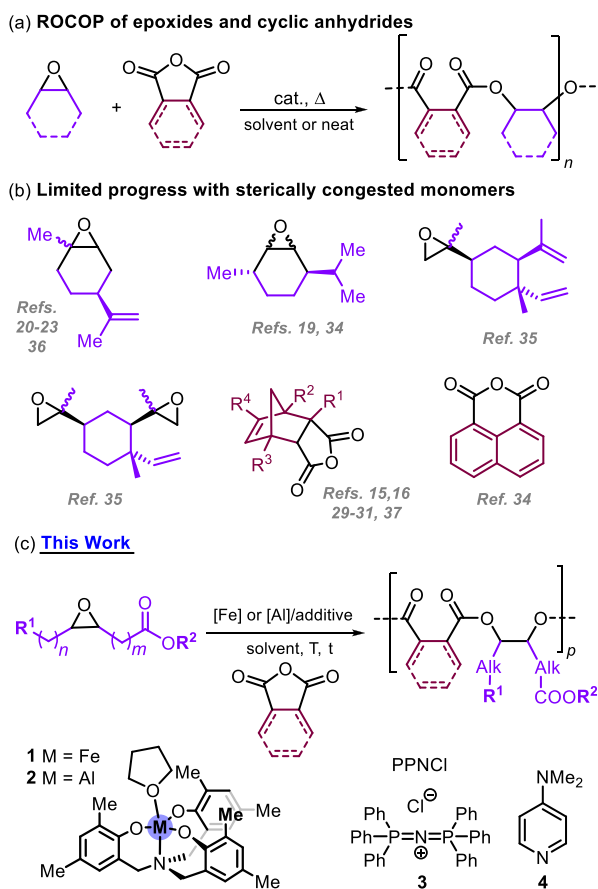
Received: February 13, 2022

Revised: March 10, 2022

Published: March 30, 2022



Scheme 1. Catalytic ROCOP of Epoxides and Cyclic Anhydrides (a), Limited Progress with Bulky Monomers (b), and This Work (c)



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

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

^aReaction 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. ^bDetermined by ¹H NMR analysis. ^cDetermined by GPC in THF calibrated with polystyrene standards, M_n values are given in kg/mol. ^dIn the presence of 0.01 equiv of BnOH. ^eIn the presence of 0.05 equiv of BnOH. ^fMOO prepared from industrial duck fat containing about 80% oleate. ^gAs for footnote f, but by using purified MOO. n.d. stands for not determined.

(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.

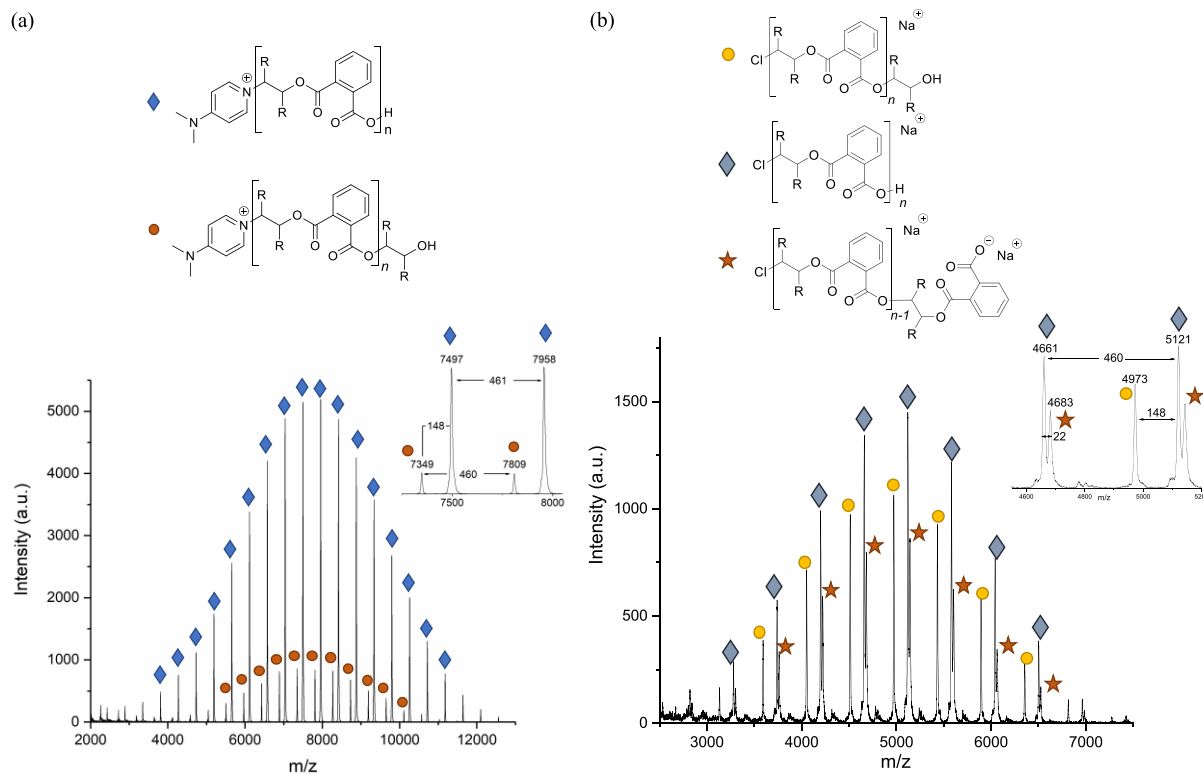


Figure 1. MALDI-ToF spectra of poly(MOO-*alt*-PA) obtained with 2/DMAP (a, entry 12, Table 1) or 1/PPNCl as catalyst (b, entry 9, Table 1).

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 ($\mathcal{D} = 1.17\text{--}1.24$) 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 ¹H NMR and GPC to determine the conversion of MOO, the selectivity of the process, and the M_n and \mathcal{D} 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 \mathcal{D} (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.

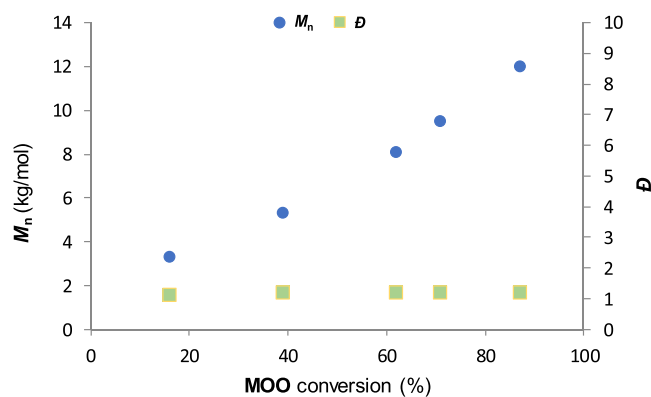


Figure 2. Copolymerization of MOO and PA mediated by 2/DMAP over time.

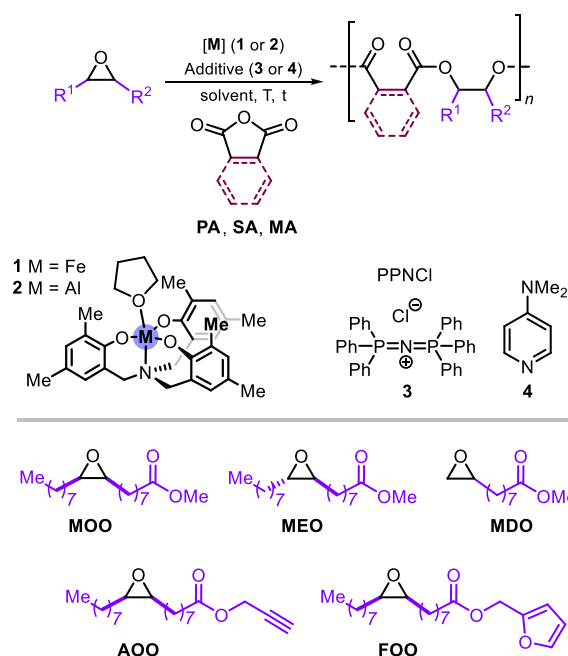
As generally observed with many ROCOP catalysts, the number-average molecular weight values M_n for the poly-(MOO-*alt*-PA) samples obtained are lower than the theoretical ones for a living system. This is often attributed to the presence of traces of protic impurities such as acid (from the hydrolysis 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 D (Table 1, entry 12) with a monomodal distribution. The use of an alcohol as a CTA in the ROCOP 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 ¹H 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 CaH₂ to remove traces of H₂O, 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	<i>t</i> (h)	yield ^b (%)	M_n/\bar{D}^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

^aReaction 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. ^bYield of the isolated polymer product after precipitation. ^cDetermined by GPC in THF calibrated with polystyrene standards, M_n values in kg/mol. ^dAOO 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 D (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 caproic 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 ($\bar{D} = 1.20$; 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

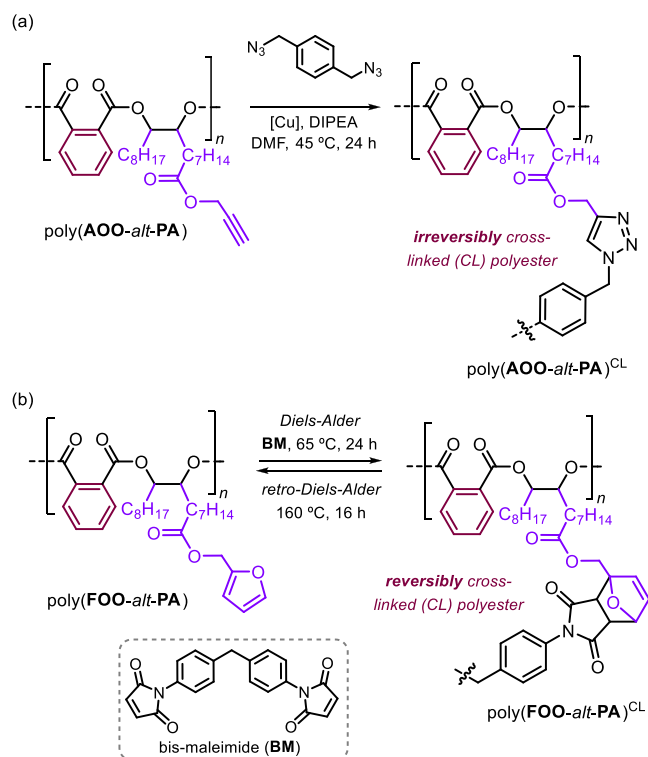
entry	polyester	M_n/\bar{D}^a	T_g^b (°C)	$T_d^{5,c}$ (°C)
1	MOO/PA	11.2/1.24	−20	265
2	MOO/SA	4.4/1.16	−45	312
3	MOO/MA	5.1/1.66	−27	280
4	MDO/PA	15.9/1.20	−5	334
5	MEO/PA	6.0/1.22	−20	289
6	AOO/PA	10.9/1.50	−22	304
7	FOO/PA	6.8/1.61	−19	269

^aData taken from Tables 1 and 2. ^bDetermined by DSC analysis at a 10 °C/min heating/cooling rate; data are from the second heating cycle. ^cFrom 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



^aFull 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 Δ(*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 *D* values

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

entry	polyester	<i>T</i> , <i>t</i> (°C, h)	<i>M</i> _n / <i>D</i> ^b
1	poly(FOO- <i>alt</i> -PA)		6.8/1.61 ^c
2 ^d	poly(FOO- <i>alt</i> -PA) ^{CL}	120, 5	<i>e</i>
3 ^f	poly(FOO- <i>alt</i> -PA) ^{CL}	120, 5	<i>e</i>
4 ^d	poly(FOO- <i>alt</i> -PA) ^{CL}	160, 16	6.6/1.40
5 ^f	poly(FOO- <i>alt</i> -PA) ^{CL}	160, 16	6.0/1.43

^aReaction conditions: poly(FOO-*alt*-PA)^{CL} (150 mg), DMF (40 wt %). ^bDetermined by GPC in THF calibrated with polystyrene standards; *M*_n values in kg/mol. ^cData from entry 9, Table 2. ^dPartially cross-linked with 15 mol % of BM. ^eNo observable conversion of the cross-linked polyester noted. ^fFully 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 *D*. 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)

AUTHOR INFORMATION

Corresponding Author

Arjan W. Kleij – Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, 43007 Tarragona, Spain; Catalan Institute of Research and Advanced Studies (ICREA), 08010 Barcelona, Spain; orcid.org/0000-0002-7402-4764; Email: akleij@icicq.es

Authors

Arianna Brandolese – Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, 43007 Tarragona, Spain

Francesco Della Monica – Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, 21100 Varese, Italy; orcid.org/0000-0001-6530-7351

Miquel A. Pericàs – Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, 43007 Tarragona, Spain; Departament de Química Inorgànica i Orgànica, Universitat de Barcelona, 08028 Barcelona, Spain; orcid.org/0000-0003-0195-8846

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.macromol.2c00321>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Cerca program/Generalitat de Catalunya, ICREA, MICINN (PID2020-112684GB-I00, PID2019-109236RB-I00, and Severo Ochoa Excellence Accreditation 2020–2023 CEX2019-000925-S). We also acknowledge support from the ERDF (European Regional Development Fund) through the POCTEFA Interreg program (EFA308/19 TRIPyr).

REFERENCES

- Keijer, T.; Bakker, V.; Slootweg, J. C. Circular Chemistry to enable a Circular Economy. *Nat. Chem.* **2019**, *11*, 190–195.
- Zuin, V. G.; Kümmerer, K. Chemistry and Materials Science for a Sustainable Circular Polymeric Economy. *Nat. Rev. Mater.* **2022**, *7*, 76–78.

- (3) Wang, Z.; Hellweg, S. First Steps Toward Sustainable Circular Uses of Chemicals: Advancing the Assessment and Management Paradigm. *ACS Sustainable Chem. Eng.* **2021**, *9*, 6939–6951.
- (4) Vollmer, I.; Jenks, M. J. F.; Roelands, M. C. P.; White, R. J.; Harmelen, T.; Wild, P.; Laan, G. P.; Meirer, F.; Keurentjes, J. T. F.; Weckhuysen, B. M. Beyond Mechanical Recycling: Giving New Life to Plastic Waste. *Angew. Chem., Int. Ed.* **2020**, *59*, 15402–15423.
- (5) Zhang, K.; Hamidian, A. H.; Tubić, A.; Zhang, Y.; Fang, J. K. H.; Wu, C.; Lam, P. K. S. Understanding Plastic Degradation and Microplastic Formation in the Environment: A Review. *Environ. Pollut.* **2021**, *274*, 116554.
- (6) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540*, 354–362.
- (7) Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116*, 1637–1669.
- (8) Stadler, B. M.; Wulf, C.; Werner, T.; Tin, S.; de Vries, J. G. Catalytic Approaches to Monomers for Polymers Based on Renewables. *ACS Catal.* **2019**, *9*, 8012–8067.
- (9) Yao, K.; Tang, C. Controlled Polymerization of Next-Generation Renewable Monomers and Beyond. *Macromolecules* **2013**, *46*, 1689–1712.
- (10) Bai, Y.; Wang, H.; He, J.; Zhang, Y. Living Polymerization of Naturally Renewable Butyrolactone-based Vinylidenes mediated by a Frustrated Lewis Pair. *Polym. Chem.* **2021**, *12*, 5548–5555.
- (11) Della Monica, F.; Kleij, A. W. From Terpenes to Sustainable and Functional Polymers. *Polym. Chem.* **2020**, *11*, 5109–5127.
- (12) Wahlen, C.; Frey, H. Anionic Polymerization of Terpene Monomers: New Options for Bio-Based Thermoplastic Elastomers. *Macromolecules* **2021**, *54* (16), 7323–7336.
- (13) Biermann, U.; Bornscheuer, U. T.; Feussner, I.; Meier, M. A. R.; Metzger, J. O. Fatty Acids and their Derivatives as Renewable Platform Molecules for the Chemical Industry. *Angew. Chem., Int. Ed.* **2021**, *60*, 20144–20165.
- (14) Nomura, K.; Binti Awang, N. W. Synthesis of Bio-Based Aliphatic Polyesters from Plant Oils by Efficient Molecular Catalysis: A Selected Survey from Recent Reports. *ACS Sustainable Chem. Eng.* **2021**, *9*, 5486–5505.
- (15) Sanford, M. J.; Peña Carrodegua, L.; Van Zee, N. J.; Kleij, A. W.; Coates, G. W. Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures. *Macromolecules* **2016**, *49*, 6394–6400.
- (16) Van Zee, N. J.; Coates, G. W. Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures. *Angew. Chem., Int. Ed.* **2015**, *54*, 2665–2668.
- (17) Thomsett, M. R.; Moore, J. C.; Buchard, A.; Stockman, R. A.; Howdle, S. M. New Renewably-Sourced Polyesters from Limonene-Derived Monomers. *Green Chem.* **2019**, *21*, 149–156.
- (18) Tschan, M. J.-L.; Brulé, E.; Haquette, P.; Thomas, C. M. Synthesis of Biodegradable Polymers from Renewable Resources. *Polym. Chem.* **2012**, *3*, 836–851.
- (19) Wambach, A.; Agarwal, S.; Greiner, A. Synthesis of Biobased Polycarbonate by Copolymerization of Menth-2-ene Oxide and CO₂ with Exceptional Thermal Stability. *ACS Sustainable Chem. Eng.* **2020**, *8*, 14690–14693.
- (20) Kindermann, N.; Cristòfol, À.; Kleij, A. W. Access to Biorenewable Polycarbonates with Unusual Glass-Transition Temperature (T_g) Modulation. *ACS Catal.* **2017**, *7*, 3860–3863.
- (21) Hauenstein, O.; Agarwal, S.; Greiner, A. Bio-Based Polycarbonate as Synthetic Toolbox. *Nat. Commun.* **2016**, *7*, 11862.
- (22) Li, C.; Sablong, R. J.; Koning, C. E. Chemoselective Alternating Copolymerization of Limonene Dioxide and Carbon Dioxide: A New Highly Functional Aliphatic Epoxy Polycarbonate. *Angew. Chem., Int. Ed.* **2016**, *55*, 11572–11576.
- (23) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405.
- (24) Thomas, C. M.; Lutz, J.-F. Precision Synthesis of Biodegradable Polymers. *Angew. Chem., Int. Ed.* **2011**, *50*, 9244–9246.
- (25) Yoshihara, S.; Mizutare, T.; Makishima, M.; Suzuki, N.; Fujimoto, N.; Igarashi, K.; Ohta, S. Potent Estrogenic Metabolites of Bisphenol A and Bisphenol B formed by Rat Liver S9 Fraction: Their Structures and Estrogenic Potency. *Toxicol. Sci.* **2004**, *78*, 50–59.
- (26) Rogers, M. E.; Long, T. E. *Synthetic Methods in Step-Growth Polymers*; Wiley-Interscience: Hoboken, NJ, 2003.
- (27) Okabayashi, R.; Ohta, Y.; Yokozawa, T. Synthesis of Telechelic Polyesters by means of Transesterification of an A2 + B2 Polycondensation-derived Cyclic Polyester with a Functionalized Diester. *Polym. Chem.* **2019**, *10*, 4973–4979.
- (28) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-Opening Copolymerization (ROCOP): Synthesis and Properties of Polyesters and Polycarbonates. *Chem. Commun.* **2015**, *51*, 6459–6479.
- (29) Longo, J. M.; Sanford, M. J.; Coates, G. W. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure–Property Relationships. *Chem. Rev.* **2016**, *116*, 15167–15197.
- (30) Sanford, M. J.; Van Zee, N. J.; Coates, G. W. Reversible Deactivation Anionic Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides: Access to Orthogonally Functionalizable Multiblock Aliphatic Polyesters. *Chem. Sci.* **2018**, *9*, 134–142.
- (31) Robert, C.; de Montigny, F.; Thomas, C. M. Tandem Synthesis of Alternating Polyesters from Renewable Resources. *Nat. Commun.* **2011**, *2*, 1596.
- (32) Martínez de Sarasa Buchaca, M.; de la Cruz-Martínez, F.; Martínez, J.; Alonso-Moreno, C.; Fernández-Baeza, J.; Tejeda, J.; Niza, E.; Castro-Osma, J. A.; Otero, A.; Lara-Sánchez, A. Alternating Copolymerization of Epoxides and Anhydrides Catalyzed by Aluminum Complexes. *ACS Omega* **2018**, *3*, 17581–17589.
- (33) Xie, R.; Zhang, Y.-Y.; Yang, G.-W.; Zhu, X.-F.; Li, B.; Wu, G.-P. Record Productivity and Unprecedented Molecular Weight for Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides Enabled by Organoboron Catalysts. *Angew. Chem., Int. Ed.* **2021**, *60*, 19253–19261.
- (34) Peña Carrodegua, L.; Martín, C.; Kleij, A. W. Semiaromatic Polyesters Derived from Renewable Terpene Oxides with High Glass Transitions. *Macromolecules* **2017**, *50*, 5337–5345.
- (35) Della Monica, F.; Kleij, A. W. Synthesis and Characterization of Biobased Polyesters with Tunable T_g by ROCOP of Beta-Element Oxides and Phthalic Anhydride. *ACS Sustainable Chem. Eng.* **2021**, *9*, 2619–2625.
- (36) Hosseini Nejad, E.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R. Catalytic Ring-Opening Copolymerization of Limonene Oxide and Phthalic Anhydride: Toward Partially Renewable Polyesters. *Macromolecules* **2013**, *46*, 631–637.
- (37) Fieser, M. E.; Sanford, M. J.; Mitchell, L. A.; Dunbar, C. R.; Mandal, M.; van Zee, N. J.; Urness, D. M.; Cramer, C. J.; Coates, G. W.; Tolman, W. B. Mechanistic Insights into the Alternating Copolymerization of Epoxides and Cyclic Anhydrides Using a (Salph)AlCl and Iminium Salt Catalytic System. *J. Am. Chem. Soc.* **2017**, *139*, 15222–15231.
- (38) For examples, refer to refs 15, 16, 29, 36, and 37.
- (39) Laserna, V.; Fiorani, G.; Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Carbon Dioxide as a Protecting Group: Highly Efficient and Selective Catalytic Access to Cyclic Cis-Diol Scaffolds. *Angew. Chem., Int. Ed.* **2014**, *53*, 10416–10419.
- (40) Sopeña, S.; Cozzolino, M.; Maquilón, C.; Escudero-Adán, E. C.; Martínez Belmonte, M.; Kleij, A. W. Organocatalyzed Domino [3 + 2] Cycloaddition/Payne-Type Rearrangement using Carbon Dioxide and Epoxy Alcohols. *Angew. Chem., Int. Ed.* **2018**, *57*, 11203–11207.

- (41) Laserna, V.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Substrate Triggered Stereoselective Preparation of Highly Substituted Organic Carbonates. *ACS Catal.* **2017**, *7*, 5478–5482.
- (42) Hayes, T.; Hu, Y.; Sanchez-Vazquez, S. A.; Hailes, H. C.; Aliev, A. E.; Evans, J. R. G. Strategies for Synthesis of Epoxy Resins from Oleic Acid Derived from Food Wastes. *J. Polym. Sci. A: Polym. Chem.* **2016**, *54*, 3159–3170.
- (43) Biermann, U.; Sehlinger, A.; Meier, M. A. R.; Metzger, J. O. Catalytic Copolymerization of Methyl 9,10-Epoxystearate and Cyclic Anhydrides under Neat Conditions. *Eur. J. Lipid Sci. Technol.* **2016**, *118*, 104–110.
- (44) He, G.-H.; Ren, B.-H.; Chen, S.-Y.; Liu, Y.; Lu, X.-B. Enantioselective, Stereoconvergent Resolution Copolymerization of Racemic cis-Internal Epoxides and Anhydrides. *Angew. Chem., Int. Ed.* **2021**, *60*, 5994–6002.
- (45) Liu, F.-P.; Li, J.; Liu, Y.; Ren, W.-M.; Lu, X.-B. Alternating Copolymerization of trans-Internal Epoxides and Cyclic Anhydrides Mediated by Dinuclear Chromium Catalyst Systems. *Macromolecules* **2019**, *52*, 5652–5657.
- (46) See for instance: Ajellal, N.; Carpentier, J.-F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. Metal-Catalyzed Immortal Ring-Opening Polymerization of Lactones, Lactides and Cyclic Carbonates. *Dalton Trans.* **2010**, *39*, 8363–8376.
- (47) Whiteoak, C. J.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Stereochemical Divergence in the Formation of Organic Carbonates Derived from Internal Epoxides. *Adv. Synth. Catal.* **2013**, *355*, 2233–2239.
- (48) Evans, R. A. The Rise of Azide-Alkyne 1,3-Dipolar Click Cycloaddition and its Application to Polymer Science and Surface Modification. *Aust. J. Chem.* **2007**, *60*, 384–395.
- (49) Liu, Z.-C.; Zuo, B.; Lu, H.-F.; Wang, M.; Huang, S.; Chen, X.-M.; Lin, B.-P.; Yang, H. A Copper(I)-Catalyzed Azide–Alkyne Click Chemistry Approach towards Multifunctional Two-Way Shape-Memory Actuators. *Polym. Chem.* **2020**, *11*, 3747–3755.
- (50) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Remendable Cross-Linked Polymeric Material. *Science* **2002**, *295*, 1698–1702.
- (51) Wang, X.; Chen, S.; Sun, Y.; Zhang, M.; Li, Y.; Li, X.; Wang, H. A Furan-bridged D- π -A Copolymer with deep HOMO Level: Synthesis and Application in Polymer Solar Cells. *Polym. Chem.* **2011**, *2*, 2872–2877.
- (52) Defize, T.; Thomassin, J.-M.; Alexandre, M.; Gilbert, B.; Riva, R.; Jérôme, C. Comprehensive Study of the Thermo-Reversibility of Diels–Alder based PCL Polymer Networks. *Polymer* **2016**, *84*, 234–242.
- (53) Defize, T.; Riva, R.; Raquez, J.-M.; Dubois, P.; Jerome, C.; Alexandre, M. Thermoreversibly Crosslinked Poly(ϵ -caprolactone) as Recyclable Shape-Memory Polymer Network. *Macromol. Rapid Commun.* **2011**, *32*, 1264–1269.
- (54) Kavitha, A. A.; Singha, N. K. Smart “All Acrylate” ABA Triblock Copolymer Bearing Reactive Functionality via Atom Transfer Radical Polymerization (ATRP): Demonstration of a “Click Reaction” in Thermoreversible Property. *Macromolecules* **2010**, *43*, 3193–3205.
- (55) Zeng, C.; Seino, H.; Ren, J.; Hatanaka, K.; Yoshie, N. Bio-Based Furan Polymers with Self-Healing Ability. *Macromolecules* **2013**, *46*, 1794–1802.
- (56) Zeng, C.; Seino, H.; Ren, J.; Hatanaka, K.; Yoshie, N. Self-Healing Bio-based Furan Polymers Cross-linked with various Bis-Maleimides. *Polymer* **2013**, *54*, 5351–5357.
- (57) Zhang, Y.; Dai, Z. H.; Han, J. R.; Li, T.; Xu, J.; Guo, B. H. Interplay between Crystallization and the Diels-Alder Reaction in Biobased Multiblock Copolyesters Possessing Dynamic Covalent Bonds. *Polym. Chem.* **2017**, *8*, 4280–4289.
- (58) He, J.; Zhang, Y.; Chen, E. Y. -X. Anionic Polymerization of Biomass-Derived Furfuryl Methacrylate: Controlling Polymer Tacticity and Thermoreversibility. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 2793–2803.