UNIVERSITY of York

This is a repository copy of Synthesis and chemoselective crosslinking of functionalized polyesters from bio-based epoxides and cyclic anhydrides.

White Rose Research Online URL for this paper: <u>https://eprints.whiterose.ac.uk/192978/</u>

Version: Published Version

Article:

Haslewood, Marcell N.D., Farmer, Thomas J. orcid.org/0000-0002-1039-7684 and North, Michael orcid.org/0000-0002-6668-5503 (2022) Synthesis and chemoselective crosslinking of functionalized polyesters from bio-based epoxides and cyclic anhydrides. Journal of Polymer Science. ISSN 2642-4169

https://doi.org/10.1002/pol.20220552

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial (CC BY-NC) licence. This licence allows you to remix, tweak, and build upon this work non-commercially, and any new works must also acknowledge the authors and be non-commercial. You don't have to license any derivative works on the same terms. More information and the full terms of the licence here: https://creativecommons.org/licenses/

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/ Revised: 3 October 2022

RESEARCH ARTICLE



Synthesis and chemoselective crosslinking of functionalized polyesters from bio-based epoxides and cyclic anhydrides

Marcell N. D. Haslewood |

Green Chemistry Centre of Excellence, University of York, York, UK

Correspondence

Thomas J. Farmer and Michael North, Green Chemistry Centre of Excellence, University of York, York YO10 5DD, UK. Email: thomas.farmer@york.ac.uk; michael.north@york.ac.uk Thomas J. Farmer 💿 | Michael North 💿

Abstract

Biomass derivable epichlorohydrin undergoes ring-opening copolymerization with either succinic or itaconic anhydride (both biosourcable) under standard laboratory conditions using metal-based or an entirely organic initiator to form highly functionalized, low molecular weight polyesters. The linear polyesters obtained from epichlorohydrin and itaconic anhydride contain both alkyl chlorides and α,β -unsaturated esters and can be crosslinked to form insoluble resins by treatment with di- to tetra-functional amines and thiols. Crosslinking with amines predominately occurs through the alkyl chlorides whilst crosslinking with thiols occurs through the α,β -unsaturated esters allowing the synthesis of insoluble polyester derived resins with complementary and controllable functionalities.

K E Y W O R D S

anhydride, bio-derivable, cross-link, epoxide, ring-opening copolymerization

1 | INTRODUCTION

Polymers are produced commercially on a scale of over 360 million metric tons per annum. They are almost entirely petrochemically derived, with less than 1% currently being produced from sustainable sources.¹ Just 9% of waste polymers are recycled, 12% are incinerated and the other 79% are disposed of on land or in the oceans² where they are a major pollutant.³ Thus, a major challenge in contemporary polymer science is to develop new, commercially viable polymers, which are sustainably sourced and degradable/recyclable at end of use so as to develop a sustainable and circular economy for polymers.⁴ This requires an integrated consideration of feedstocks, production methodology and design for degradation/reuse.

Polyesters are intrinsically degradable at end of life by hydrolysis of their constituent ester bonds. As such, they are more recyclable than other classes of widely used polymers.⁵ The main commercial synthesis of polyesters involves a thermally induced step-growth, condensation polymerization between a diol and a diacid or diester (Scheme 1A)⁶ with a well-known example being the production of poly(ethylene terephthalate) (PET) which is widely used in textiles and packaging. Since many diacids and diols are readily available from biomass, it should be possible to prepare sustainably sourced polymers in this way. However, the harsh thermal conditions limit the functional groups that can be present in the monomers. For example, the geminal alkene of itaconic is known to undergo undesirable isomerization or Ordelt saturation, limiting the chain length when using this bio-based monomer in conventional polycondensations.⁷

An alternative route for the synthesis of polyesters involves the step-growth, ring-opening, alternating copolymerization (ROCOP) of epoxides and cyclic anhydrides (Scheme 1B).⁸ This is a catalyzed process, which occurs at

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes. © 2022 The Authors. *Journal of Polymer Science* published by Wiley Periodicals LLC.





SCHEME 1 Synthesis of polyesters by (A) condensation polymerization and (B) ring-opening, alternating copolymerization



SCHEME 2 Mechanism of ring opening, alternating copolymerization showing how water induces chain-transfer

lower temperatures than the condensation polymerization, so it is more compatible with functionalized monomers. Cyclic anhydrides are readily prepared from diacids and epoxides can be formed by a number of routes, including the oxidation of alkenes, so the ROCOP route to polyesters is also compatible with sustainably sourced monomers. When carried out under ideal conditions, ROCOP is a living polymerization process, which is capable of producing polymers with narrow molecular weight distributions. However, due to the mechanism of this polymerization (Scheme 2), it is very susceptible to chain-transfer by adventitious moisture in the reaction mixture, which reduces the molecular weight of the polymer and broadens the molecular weight distribution. As a result, ROCOP is typically carried out under rigorously inert and anhydrous conditions involving the use of a glove box. This is a major obstacle to its commercialization.

In this work we demonstrate for the first time that ROCOP can be initiated either by metal(salophen)



FIGURE 1 Structures of initiators 1–3 and PPNCl cocatalyst 4.

complexes or by dicyclohexylurea (both in the presence of PPNCl (bis[triphenylphosphine]iminium chloride) as a cocatalyst) under standard laboratory conditions without the use of glove box. In addition to petrochemically derived monomers, the methodology is shown to be compatible with functionalized epoxides and anhydrides obtainable from biomass.^{9–13} The resulting polyesters have lower molecular weights than the theoretical values due to chain-transfer. However, the highly functionalized, biomass derivable, low molecular weight polyesters are then shown to undergo crosslinking reactions with unprecedented chemoselectivity when treated with polyfunctional amines and thiols, leading to functionalized, insoluble, crosslinked resins with potential applications in coatings, adhesives and composites. Amine crosslinkers are shown to preferentially react by substitution reactions with alkyl chlorides within the polyester whilst thiol crosslinkers preferentially react by addition to α , β -unsaturated ester units within the same polyester.

2 | RESULTS AND DISCUSSION

Many metal complexes have been reported to initiate the ROCOP of epoxide and cyclic anhydrides.⁸ Amongst these, metal(salophen) complexes have the advantages of being highly active, readily prepared and possessing good tolerance to air and moisture. Salophen complexes of aluminium,¹⁴ cobalt,¹⁵ chromium,^{11,16} manganese¹⁷ and iron¹⁸ have all been used with chromium(salophen) complexes generally exhibiting highest activities. Therefore, chromium(salophen) complex 1 and aluminum(salophen) complex 2 were selected as initiators for this study (Figure 1). Whilst chromium-based complex 1 was expected to be the most active, aluminum complex 2 would have the advantage of not leaving colored metal residues in the polymer. There is also growing interest in metal-free initiators for ROCOP of epoxide and cyclic anhydrides.⁸ Amongst the systems reported, the use of dicyclohexylurea **3** as a ROCOP initiator¹⁹ appeared particularly attractive due to its stability to air and moisture and its ready



FIGURE 2 Structures of epoxides **5a,b** and cyclic anhydrides **6a-c**

availability as a by-product of many ester and amide bondforming reactions.²⁰ Therefore, in this study initiators 1-3were all utilized. These initiators all require the use of PPNCl **4** as a co-catalyst to provide the nucleophile needed to initiate the ROCOP process.

ROCOP reactions using initiators 1-3 were carried out at 100 °C in sealed, oven dried reaction vials under a nitrogen atmosphere and (where appropriate) using dried solvent though not employing a glove box or other specialized containment facilities. Initial studies to determine the viability of ROCOP initiated by initiators 1-3under these conditions were carried out using the widely used monomers cyclohexene oxide **5a** and phthalic anhydride **6a** (Figure 2) with results being shown in Table 1.

Entries 1–5 of Table 1 show the results of control experiments in which the initiator and/or co-catalyst were omitted. Entry 1 shows that in the absence of both an initiator (1-3) and co-catalyst (4), no polymerization occurs, whilst entry 2 shows that co-catalyst 4 is able to produce some polyester from monomers **5a** and **6a** even in the absence of an initiator.²¹ Entries 3–5 show that aluminum(salophen) complex 2 was totally inactive in the absence of co-catalyst 4 whilst initiators 1 and 3 did produce small amounts of polymer (<20%) even in the absence of co-catalyst 4.

Entries 6-11 of Table 1 show the results of polymerization reactions carried out using each of initiators 1-3 in the presence of an equimolar amount of co-catalyst 4. Each polymerization was carried out under both solvent free conditions and in toluene to control the viscosity of the reaction mixture. The reactions in toluene were slower, but better controlled, giving polyester with a higher molecular weight than polymerizations carried out under solvent free conditions (compare entries 6 and 7; 8 and 9; 10 and 11). Chromium(salophen) complex 1 was the most active initiator under both reaction conditions (entries 6 and 7) and when used in toluene also gave the polyester with the highest molecular weight. Initiators 2 and 3 had virtually identical activities (entries 8-11), though when used in toluene, aluminum(salophen) complex 2 produced a polymer with a particularly low percentage of ether bonds (entry 9). Literature data¹⁰ for the polymerization of monomers 5a and 6a under rigorously anhydrous conditions using initiators 1 and 2 with

co-catalyst **4** at the same 1:1:250:250 ratio of initiator to co-catalyst to monomers suggests that polymer molecular weights of 11,000 to 13,600 Da are obtainable. These are about an order of magnitude higher than the polymer molecular weights obtained under the conditions used in this study (Table 1, entries 6–7), showing that chaintransfer due to adventitious moisture is occurring and reduces the polymer molecular weight. Notably however, the theoretical polymer molecular weight under these conditions is 61,500 Da showing that chain-transfer cannot be totally avoided. The same conclusions apply to reactions initiated by DCHU **3**, though in this case the literature data¹⁹ used different initiator to monomer ratios.

Having demonstrated that ROCOP was feasible using petrochemically derived monomers 5a and 6a under these reaction conditions, the use of biomass derivable monomers was investigated. Epichlorohydrin 5b is a highly functionalized epoxide which is now prepared industrially from the glycerol byproduct of biodiesel production.²² Succinic anhydride **6b** is producible from succinic acid which is produced commercially by sugar fermentation²³ and itaconic anhydride 6c is a functionalized anhydride available either from itaconic acid (produced by fungal fermentation of sugars²⁴) or by thermolysis of citric acid.²⁵ Therefore, the ROCOP of each of monomers **5b** and **6b,c** with the complementary petrochemically derived monomer 5,6a was initially investigated, under the same reaction conditions used for the polymerization of monomers 5,6a, giving the results shown in Table 2.

Entries 1-3 of Table 2 are control experiments showing that epichlorohydrin 5b would not undergo homopolymerization to form a polyether under the reaction conditions. Entries 4-9 show the results obtained for the polymerization of cyclohexene oxide 5a with succinic anhydride 6b. For this pair of monomers, initiators 1 and 3 gave polymers with almost identical molecular weights (entries 4, 5, 8, and 9), but chromium(salophen) initiator 1 gave the highest yields and the lowest amount of ether linkages within the polymer, especially when the reaction was carried out in toluene (entry 5). The polymer molecular weights obtained using initiators 1 and 3 with the 5a,6b monomer pair are higher than those obtained for the polymer prepared from monomers 5a,6a, especially considering that the theoretical molecular weight for the polymer in this case is just 49,500 Da. The polymer molecular weights obtained with initiator 1 are also fully consistent with those previously reported (1300-1600 Da) for the polymerization of these monomers at the same initiator to monomer ratio.¹⁵ For reactions using initiator 3, polymers with molecular weights of 2500-3300 Da have been reported, but at different monomer to initiator ratios.19

TABLE 1 Ring opening, alternating copolymerization of monomers 5a and 6a using initiators 1–3

Entry	Initiator (ratio) ^a	Solvent	Time (min)	Conversion (%) ^b	Ether (%) ^c	M_n (kg mol ⁻¹) (D) ^d
1	None (0:0:250:250)	None	60	0	0	nd
2	None (0:1:250:250)	None	60	48	12	nd
3	1 (1:0:250:250)	None	60	9	48	nd
4	2 (1:0:250:250)	None	60	0	0	nd
5	3 (1:0:250:250)	None	60	19	18	nd
6	1 (1:1:250:250)	None	15	76	10	0.65 (1.12)
7	1 (1:1:250:250)	Toluene	60	79	14	1.76 (1.04)
8	2 (1:1:250:250)	None	15	64	24	1.32 (1.09)
9	2 (1:1:250:250)	Toluene	60	62	5	1.68 (1.08)
10	3 (1:1:250:250)	None	30	66	22	0.56 (1.16)
11	3 (1:1:250:250)	Toluene	60	63	17	1.56 (1.08)

^aMolar ratio of initiator (1-3):PPNCl (4):epoxide (5a):anhydride (6a).

^bConversion (of anhydride **5a**) was determined by ¹H NMR spectroscopic analysis of the polymerization reaction mixture.

^cEther (%)was determined by ¹H NMR spectroscopic analysis using the CH resonances at 5.1–5.2 ppm (ester) and 3.4–3.7 ppm (ether).

^dMeasured by GPC in THF using polystyrene standards. The theoretical value of M_n is 61.5 kg mol⁻¹ in all cases.

The ROCOP of cyclohexene oxide **5a** and itaconic anhydride **6c** with all three initiators was best carried out in toluene (Table 2, entries 10–15). Under these conditions, all three initiators gave high yields of the polymer and using initiator **1**, a polymer with an average molecular weight of 7300 Da was obtained (compared to a theoretical value of 52,500 Da). ROCOP of this pair of monomers has not previously been reported.

Epichlorohydrin 5b and phthalic anhydride 6a underwent ROCOP initiated by each of initiators 1-3 as detailed in Table 2, entries 16-21. The best results were obtained using chromium(salophen) complex 1 as initiator (entries 16,17) which gave high yields of polymer with molecular weights of 8900-11,700 Da (the theoretical value is 60,125 Da). Initiators 2 and 3 gave polymers with very similar properties (entries 18-21), though the yields were better with aluminum(saleophen) complex 2 than with DCHU 3. As expected based on the control experiments in entries 1-3 of Table 2 and on literature precedent,²⁶ none of the **5b,6a** copolymers showed any evidence of ether linkages within their structures. The ROCOP of this pair of monomers using initiators 1-3 has not previously been reported, but the polymer has been prepared with other catalyst systems.²⁶

The polymerizations shown in Table 2 appeared highly promising with polymers generally being prepared in high yield and with molecular weights higher than those obtained for the **5a,6a** monomer system. The absence of any polyether in polymers derived from epichlorohydrin **5b** is beneficial and chromium(salophen) complex **1** appears to be the most effective initiator, with initiators **2** and **3** having very similar reactivity. Notably, all three initiators were compatible with the additional functionalities present in monomers **5b** and **6c**. Therefore, the synthesis of completely bioderivable polyesters by ROCOP of monomers **5b** and **6b,c** was undertaken with the results shown in Table 3.

The combination of monomers 5b and 6b gave high monomer conversions with all three initiators (Table 3, entries 1–6). However, the polymer molecular weights were rather low (990-1530 Da) compared to the theoretical molecular weight of 48,125 Da. This polyester has previously been prepared by ROCOP using other initiators and different monomer to initiator ratios.5,26 In contrast, the polymerization of epoxide 5b with the more functionalized anhydride 5c was initiator dependent. Chromium(salophen) complex 1 (and aluminum(salophen) complex 2 in the absence of solvent) gave high yields of polymer (entries 7-9) whilst DCHU 3 (and aluminum(salophen) complex 2 in toluene) gave only low to moderate yields of polymer (entries 10-12). The polymers generally had higher molecular weights (up to 2230 Da compared to a theoretical value of 51,125 Da) than those obtained from 5b and 6b. This combination of monomers does not appear to have been previously used in ROCOP reactions.

All of the linear polyesters were analyzed by ¹H NMR spectroscopy and two informative examples are shown in Figures 3 and 4. The polymer obtained from epichlorohydrin **5b** and phthalic anhydride **6a** gave a simple ¹H NMR spectrum (Figure 3) which allowed the end-group to be identified (signals d, e and g) and showed that virtually all of the polymer chains were terminated by a hydroxyl group arising from chain-transfer. In contrast,

Entry	Epoxide	Anhydride	Initiator ^a	Solvent	Time (min)	Conversion (%) ^b	Ether (%) ^c	M_n (kg mol ⁻¹) ^d	Đ ^đ	Theoretical M_n (kg mol ⁻¹)
1	5b	None	1 ^e	None	60	0	0	nd	nd	
2	5b	None	2 ^e	None	60	0	0	nd	nd	
3	5b	None	3 ^e	None	60	0	0	nd	nd	
4	5a	6b	1	None	45	82	10	2.27	1.00	49.5
5	5a	6b	1	Toluene	60	93	5	2.28	1.00	49.5
6	5a	6b	2	None	60	45	24	*	*	49.5
7	5a	6b	2	Toluene	60	51	17	*	*	49.5
8	5a	6b	3	None	60	62	36	2.17	1.00	49.5
9	5a	6b	3	Toluene	60	30	25	2.18	1.00	49.5
10	5a	6c	1	None	45	96	**	4.37	1.51	52.5
11	5a	6c	1	Toluene	120	>99	**	7.37	2.53	52.5
12	5a	6c	2	None	45	79	**	*	*	52.5
13	5a	6c	2	Toluene	120	99	**	3.29	2.16	52.5
14	5a	6c	3	None	45	92	**	1.38	2.28	52.5
15	5a	6c	3	Toluene	120	90	**	1.45	2.27	52.5
16	5b	6a	1	None	15	90	0	11.68	1.80	60.1
17	5b	6a	1	Toluene	60	97	0	8.93	1.31	60.1
18	5b	6a	2	None	30	90	0	5.89	1.26	60.1
19	5b	6a	2	Toluene	60	89	0	6.35	1.37	60.1
20	5b	6a	3	None	45	69	0	5.41	1.21	60.1
21	5b	6a	3	Toluene	60	78	0	7.67	1.26	60.1

TABLE 2 Ring-opening, alternating copolymerization of biomass derivable monomers 5b and 6b,c with petrochemically derived monomers 5,6a using initiators 1–3

Note: * indicates polymer failed to precipitate during purification and so could not be analyzed by GPC. ** indicate Could not be determined due to signal overlap.

Abbreviation: nd, not determined.

^aMolar ratio of initiator:PPNCl:epoxide:anhydride was 1:1:250:250 unless stated otherwise.

^bConversion (of anhydride **5a**) was determined by ¹H NMR spectroscopic analysis of the polymerization reaction mixture.

^cEther (%) was determined by ¹H NMR spectroscopic analysis using the CH resonances at 5.1–5.2 ppm (ester) and 3.4–3.7 ppm (ether).

^dMeasured by GPC in THF using polystyrene standards.

^eMolar ratio of initiator:PPNCl:epoxide:anhydride was 1:1:250:0.

TABLE 3 Ring-opening, alternating copolymerization of monomers **5b** and **6b,c** using initiators **1–3**

Entry	Anhydride	Initiator ^a	Solvent	Time (min)	Conv. (%) ^b	M_n (kg mol ⁻¹) (\mathcal{D}) ^c
1	6b	1	None	60	95	1.53 ^d (1.64)
2	6b	1	Toluene	120	>99	1.51 ^d (1.38)
3	6b	2	None	60	97	1.02^{d} (1.13)
4	6b	2	Toluene	120	91	1.06 ^d (1.19)
5	6b	3	None	60	96	0.99 ^d (1.12)
6	6b	3	Toluene	120	89	1.21 ^d (1.26)
7	6с	1	None	120	99	_e
8	6с	1	Toluene	120	>99	2.23 ^f (1.29)
9	6с	2	None	120	90	$1.30^{f}(1.01)$
10	6с	2	Toluene	120	38	$1.41^{f}(1.05)$
11	6c	3	None	120	60	$1.68^{f}(1.15)$
12	6c	3	Toluene	120	29	$1.61^{f}(1.14)$

^aMolar ratio of initiator:PPNCl:epoxide:anhydride was 1:1:250:250.

^bConversion (of anhydride) was determined by ¹H NMR spectroscopic analysis of the polymerization reaction mixture.

^cMeasured by GPC in THF using polystyrene standards.

^dThe theoretical M_n is 48.1 kg mol⁻¹.

^ePolymer was insoluble in THF.

^fThe theoretical M_n is 51.1 kg mol⁻¹.





the ¹H NMR spectrum of the polymer obtained from epichlorohydrin **5b** and itaconic anhydride **6c** (Figure 4) was more complex. It is well known¹³ that the double bond in itaconates is prone to isomerization to form mesaconate and/or citraconate units. Evidence of this is clearly present in Figure 4 as in addition to the two expected alkene signals (a and c at 5.8 and 6.4 ppm) for itaconate units, an additional signal (b) is present at 5.9 ppm, consistent with a citraconate unit.²⁷

Itaconate units are also prone to other side reactions including radical-crosslinking and Ordelt saturation: an oxo-Michael addition of hydroxyl-terminated polymer chains onto the α , β -unsaturated ester units.¹³ Evidence for these processes was also seen in polymerizations



FIGURE 4 ¹H NMR spectrum in $CDCl_3$ of the copolymer obtained from epoxide **5b** and anhydride **6c**

involving itaconic anhydride. Thus in the ¹H NMR spectra of the polymers (Figure 4), the integral of the aliphatic groups relative to the alkenes was higher than expected. It was also found that if the polymerization reaction times were extended beyond 240 min then gelation of the reaction mixture was observed and a soft, rubbery, insoluble resin was formed, typical of directly crosslinked itaconate polyesters created by radical crosslinking.²⁸

All the polyesters were analyzed by DSC to determine their glass transition temperatures (T_g) , with selected examples given in Appendix S1. Melting temperatures were seldom observed, indicating the samples to be predominately amorphous. Most of the polyesters had T_g 's of



FIGURE 5 Potential post-polymerization modifications and structures of multifunctional nucleophiles **7a–d**

30–50 °C, giving them glass transition temperatures similar to polymers currently use as films, coatings and in packaging.²⁹ Where data had been previously reported, the T_g 's were within 10 °C of the literature values.^{26,30} Polymers prepared from epichlorohydrin **5b** and succinic anhydride **6b** (Table 3, entries 1–6) had lower T_g 's of –18 to –4 °C, reflecting the lack of rigidity or sterically demanding groups in this polymer backbone. Correspondingly, polyesters derived from cyclohexene oxide **5a** and phthalic anhydride **6a** (Table 1, entries 7 and 11) had higher T_g 's (75–110 °C) due to the rigidity of the backbone of this polymer.

The highly functionalized nature of the linear polyesters derived from epichlorohydrin 5b and/or itaconic anhydride 6c gave them the potential to undergo postpolymerization modification and in particular to undergo crosslinking reactions leading to insoluble thermoset resins. The polyester derived from both epichlorohydrin and itaconic anhydride (Table 3, entries 7-12) was particularly interesting in this respect as it contains two complementary units capable of reacting with nucleophiles. Thus, as shown in Figure 5, the α , β -unsaturated ester units can undergo addition reactions whilst the primary alkyl halides can undergo substitution reaction. Whilst post-polymerization modification via Michael additions onto itaconate units is well known,³¹ there are no previous reports of post-polymerization modification via nucleophilic substitution of epichlorohydrin derived units, though the known surface modification of polyvinyl chloride by nucleophilic substitution reactions³² provides precedent for the feasibility of this process.

Four polyfunctional nucleophiles (7a-d) were selected to act as crosslinking agents for the

7

epichlorohydrin and itaconic anhydride derived polyester prepared under solvent free conditions using organoinitiator 3 and co-catalyst 4. Crosslinkers 7a,b contain nucleophilic nitrogen atoms whilst crosslinkers 7c,d contain nucleophilic sulfur atoms. To avoid chain cleavage via pyrolidone formation³³ only secondary amine crosslinkers were selected. Piperizine 7a has been widely used for step-growth aza-Michael polycondensations,³⁴ and was recently shown to readily react with itaconate esters with high selectivity.³⁵ Triamine 7b was chosen for its longer spacing between the reactive amines. Although this amine has been shown to undergo aza-Michael additions to acrylates, this study represents its first use as an aza-Michael cross-linker.³⁶ Both thiols 7c and 7d have previously been used as nucleophilic cross-linkers.³⁷ Crosslinking reactions were carried out using a literature procedure³¹ for 16 h at 70 °C either solvent-free or in DMF under an inert atmosphere using stoichimometric amounts of 7a-d, assuming that 7a-c were bifunctional and 7d was tetrafunctional. Results are presented in Table 4.

Entries 1 and 2 of Table 4 are control experiments carried out in the absence of any crosslinker to investigate the propensity of the linear polyester to undergo radical polymerization and/or Ordelt saturation under the crosslinking reaction conditions.¹³ When carried out under solvent-free conditions, no insoluble material formed under these conditions (entry 1) and when DMF was used as solvent, just 7% formation of insoluble polymer occurred (entry 2), showing that self-crosslinking reactions occurred to a negligible extent under the reaction conditions. Entries 3-6 show the results obtained with nitrogen based crosslinkers 7a,b. Both crosslinkers gave good yields of insoluble resin, with piperazine 7a being more effective than linear triamine 7b. In both cases, use of DMF as a solvent was beneficial both to the vield of resin and the amount of nitrogen incorporated into it with both crosslinkers able to incorporate close to the theoretical amount of nitrogen. The thiol based crosslinkers gave lower yields of insoluble polymer (entries 7-10), with only crosslinker 7d in DMF able to give a good yield of material. The amount of sulfur incorporated into these polymers was significantly lower than the theoretical maximum values suggesting either that the reactions are not complete or that the thiols have initiated other crosslinking reactions such as oligomerization of the α,β -unsaturated ester groups.

Thermogravimetric analysis was carried out on five of the crosslinked resins (Table 4, entries 4–7 and 10) to investigate their thermal behavior. The linear precursor polyester was also analyzed and found to lose 10% of its mass at 286 °C. This is very similar to the 282 °C found for the resin crosslinked with tetrathiol **7d** (entry 10).

TABLE 4 Ring-opening, alternating copolymerization of monomers 5b and 6a,c using initiators 1–3

Entry	Crosslinker	Solvent	Yield (%) ^a	N or S (%)	Theoretical N or S (%) ^b	<i>T</i> _{D10} (°C) ^c
1	None	None	0	nd	0	nd
2	None	DMF	7	nd	0	nd
3	7a	None	90	2.5 N	5.7–6.6 N	nd
4	7a	DMF	95	5.0 N	5.7–6.6 N	187
5	7b	None	77	6.6 N	7.2–8.3 N	177
6	7b	DMF	83	7.2 N	7.2–8.3 N	171
7	7c	None	30	7.3 S	10.8–12.3 S	134
8	7c	DMF	39	3.5 S	10.8–12.3 S	nd
9	7d	None	1	3.1 S	9.8–11.0 S	nd
10	7d	DMF	79	5.2 S	9.8–11.0 S	282

^aMass yield of insoluble material obtained.

^bA range is quoted as addition and substitution reactions give different theoretical values.

°Temperature at which the crosslinked resin loses 10% of its mass determined by TGA.



FIGURE 6 TGA traces for the linear polyester of monomers **5b** and **6c** (red line) and the derived resin crosslinked with piperazine **7a** in DMF (blue curve)

However, the other crosslinked materials were found to lose 10% mass at a much lower temperature (134–187 °C, entries 4–6). A representative thermogravimetric analysis (TGA) trace is presented in Figure 6 and shows that the mass loss occurs in three stages. Approximately 20% mass is lost between 100 and 245 °C, followed by 40% mass loss between 245 and 325 °C and finally 24% mass loss above 325 °C. The two higher temperature mass losses are consistent with decomposition of the polyester chains, suggesting that the lowest temperature mass loss corresponds to the loss of the crosslinker by retro-Michael or amine dealkylation reactions.

To fully understand the nature of the crosslinking, the insoluble resins were analyzed by FT-IR and solid state ¹³C NMR spectroscopy. As shown in Figure 7, the linear polyester obtained from epoxide **5b** and anhydride **6c** showed a strong IR band at 1726 cm^{-1} corresponding to the ester carbonyl stretch and a medium intensity



FIGURE 7 Extracts of the infrared spectra of the linear polyester (black) and resins crosslinked with **7a** (pale blue), **7b** (dark blue), **7c** (pale red) or **7d** (dark red)

band at 1651 cm⁻¹ corresponding to the itaconate carbon–carbon double bond stretch. The ester carbonyl band was also present in the spectra of the insoluble resins obtained from all four crosslinkers, showing that the polyester backbone had survived the crosslinking process. The IR spectra of resin crosslinked with amines **7a**,**b** also retained the carbon–carbon double bond stretch, indicating that crosslinking had occurred predominantly or exclusively by reaction with the alkyl chloride groups. In contrast, no carbon–carbon double bond stretch was apparent in the IR spectra of resins crosslinked by thiols **7c**,**d**, indicating that in this case, crosslinking had

FIGURE 8 Extract of the solution state ¹³C NMR spectrum of the linear polyester (bottom) and the solid state ¹³C NMR spectra of the resins obtained after crosslinking with **7b** (middle) and **7d** (top)



occurred predominantly or exclusively by Michael addition to the α , β -unsaturated esters. Thus, the crosslinking is a chemoselective process which can be controlled to produce a resin containing either α , β -unsaturated esters (amine crosslinkers) or alkyl halides (thiol crosslinkers).

This analysis was supported by ¹³C NMR analysis of the polymers. Figure 8 shows extracts of the solution state ¹³C NMR spectrum of the linear polyester obtained from epoxide **5b** and anhydride **6c** and the solid state ¹³C NMR spectra of the resins obtained by crosslinking this polymer with triamine **7b** and tetrathiol **7d**. The linear polyester shows signals corresponding to ester carbonyls (160-175 ppm) and alkenes (115-150 ppm). The resin obtained after crosslinking with triamine 7b shows broad signals corresponding to both of these carbon environment, whilst the resin obtained after crosslinking with tetrathiol 7d shows only a signal corresponding to the carbonyl groups. This confirms the analysis made on the basis of the IR spectra and shows that the thiol based crosslinking has gone to completion, so processes such as oligomerization of the α,β -unsaturated ester groups must have occurred to account or the lower than expected sulfur incorporation.

3 | CONCLUSION

This work has clearly demonstrated that linear polyesters wholly of partially derived from functionalized biomassderivable anhydrides and epoxides can be prepared under scalable standard laboratory conditions without the need for specialized equipment. Either metal(salophen) complexes or dicyclohexylurea can be used as the polymerization initiator. Chain transfer involving adventitious water occurs so that the polymer chains are terminated by hydroxyl and carboxylic acid groups, but soluble, linear polymers with number average molecular weights up to 11,700 can still be obtained. The functional groups present in the linear polymers allows them to be crosslinked to form thermosetting resins by treatment with polyfunctionalized nitrogen or sulfur based nucleophiles. Interestingly, the crosslinking is chemoselective with amines reacting predominantly by substitution at the alkyl chloride groups, whilst thiols react predominantly by addition to the α , β -unsaturated esters. These discoveries will facilitate the further development and application of biomass derived polyesters prepared by ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides.

4 | EXPERIMENTAL SECTION

Initiators **1** and **2** were prepared by literature procedures.³⁸ Initiator **3**, co-catalyst **4** and all epoxides and anhydrides were commercially available and used as received. Gel Permeation Chromatography was carried out using a set of 3 analytical columns (300×8 mm, particle diameter 5 µm) of 1000, 10^5 and 10^6 Å pore sizes, plus a guard column, installed in a PSS SECcurity GPC system. Elution was with stabilized THF at 1 ml min⁻¹ with a column temperature of 23 °C and detection by refractive index. 20 µl of a 1 mg ml⁻¹ sample in THF was injected for each measurement and eluted for 40 min. Calibration was carried out in the molecular weight range $400-2 \times 10^6$ Da using Ready-Cal polystyrene standards.

4.1 | General procedure for the synthesis of linear polyesters

All polymerization reactions were performed at 100 °C for 1 hour with a [initiator]: [co-initiator]: [epoxide]: [anhydride] ratio of 1:1:250:250 where $1 = 20 \mu mol$ unless stated otherwise in Tables 1-3. To an oven-dried 5 ml sample vial and magnetic stirrer bar were added initiator, co-catalyst and anhydride and the vessel was sealed and purged with nitrogen. Epoxide was added, along with toluene (1 ml) if the reaction was performed in solution. The vial was heated to the desired temperature. After the specified reaction time, or when viscosity had increased to a point where stirring was no longer effective, the reaction was cooled to room temperature, exposed to air and an aliquot was taken for ¹H NMR analysis. The polymer was purified by dissolving in the minimum amount of CH₂Cl₂ and precipitating into a 10-fold excess of cold methanol or hexane twice. The solid polymer was separated and dried under vacuum to a constant weight.

4.1.1 | Poly(5a-6a)

 $v_{\rm max}$ (KBr, cm⁻¹): 2932, 2860, 1717, 1596, and 1578 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃): 1.41 (2H, br, CH₂), 1.51 (2H, br, CH₂), 1.77 (2H, br, CH₂), 2.23 (2H, br, CH₂), 5.14 (2H, br, 2 × OCH), 7.3–7.8 (4H, m, 4 × ArH), peaks corresponding to polyether blocks are visible at 2.1, 3.6 and 4.9 ppm; $\delta_{\rm C}$ (75 MHz, CDCl₃): 23.4, 30.0, 32.5, 74.6, 74.8, 79.98, 128.8, 131.0, 132.1, and 166.7.

4.1.2 | Poly(5a-6b)

 $v_{\rm max}$ (KBr, cm⁻¹): 2938, 2860 and 1724 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃): 1.37 (4H, br, 2 × CH₂), 1.73 (2H, br, CH₂), 2.01

(2H, br, CH₂), 2.60 (4H, br, 2 \times COCH₂), 4.81 (2H, br, 2 \times OCH); $\delta_C(75$ MHz, CDCl₃): 23.3, 29.2, 30.0, 73.7, and 171.7.

4.1.3 | Poly(5a-6c)

 v_{max} (KBr, cm⁻¹): 2927, 2860, 1766, 1724 and 1650 cm⁻¹; δ_{H} (300 MHz, CDCl₃): 1.30 (br, CH₂/CH₃), 1.69 (br, CH₂), 2.01 (br, CH₂), 2.0–3.5 (br, COCH₂), 4.5–5.0 (br, OCH), 5.6–5.9 (br, =CH₂), 6.27 (br, =CH₂).

4.1.4 | Poly(5b-6a)

 $v_{\rm max}$ (KBr, cm⁻¹): 2960, 1722, 1599 and 1579 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃): 1.80 (1H, br, OH), 3.81 (2H, br, CH₂Cl), 4.59 (2H, br, OCH₂), 5.53 (1H, br, OCH), 7.54 (2H, m, 2 × ArH), 7.73 (2H, m, 2 × ArH); ¹³C NMR (75 MHz, CDCl₃): 42.1, 63.5, 71.5, 129, 1, 129.2, 131.1, 131.6, 131.7, and 166.5.

4.1.5 | Poly(5b-6b)

 $v_{\rm max}$ (KBr, cm⁻¹): 2964 and 1732 cm⁻¹; $\delta_{\rm H}$ (300 MHz, CDCl₃): 2.68 (4H, s, 2 × CH₂CO), 2.87 (1H, br, OH), 3.6– 3.8 (2H, m, CH₂Cl), 4.2–4.5 (2H, m, CH₂), 5.24 (1H, m, CH); ¹³C NMR (75 MHz, CDCl₃): 28.8, 28.9, 42.2, 62.7, 70.8, 171.4, and 171.7.

4.1.6 | Poly(5b-6c)

 v_{max} (KBr, cm⁻¹): 3515, 2964, 1764, 1724, and 1651 cm⁻¹; TGA: T_{D10} 286 °C; δ_{H} (300 MHz, CDCl₃): 2.07 (br, CH₂), 3.5–3.8 (br, CH₂Cl), 4.0–4.6 (br, OCH₂), 5.1–5.4 (br, OCH), 5.8 (br, C=CH₂), 6.4 (br, C=CH₂), peaks corresponding to citraconate units are also visible at 2.1 (bt, CH₃) and 5.9 (br, C=CH) ppm; ¹³C NMR (75 MHz, CDCl₃): 20.7, 20.9, 42.2, 45.4, 45.9, 62.9, 66.3, 69.3, 71.0, 119.6, 120.4, 130.2, 132.8, 143.5, 146.7, 163.8, 164.4, 165.8, 168.2, 168.6, and 170.2, spectrum shows multiple peaks due to the presence of both itaconate and citraconate units.

4.2 | General procedure for crosslinking

All crosslinking reactions were performed at 70 °C for 16 h with a [difunctional crosslinker]: [polymer repeat units] stoichiometric ratio of 1: 2 or [tetrafunctional crosslinker]: [polymer repeat units] ratio of 1: 4, where 1 = 0.490 mmol unless stated otherwise. To an

HASLEWOOD ET AL.

oven-dried 5 ml sample vial were added polymer and cross-linker and the vessel was sealed and purged with nitrogen. If the reaction was performed in solution, DMF (0.1 ml) was added and the reaction heated to the desired temperature. After the specified reaction time, the reaction was cooled to room temperature and exposed to air. Unreacted linear polymer was removed by adding CH_2Cl_2 (5 ml) and stirring overnight, then decanting the solute and drying the remaining solid under vacuum to a constant weight to give the crosslinked resin.

4.2.1 | 7a crosslinked resin

 $v_{\rm max}$ (KBr, cm⁻¹): 3400, 2956, 2821, 2472, 1730, and 1619 cm⁻¹; TGA: $T_{\rm D10}$ 187 °C; solid state ¹³C NMR (100 MHz): 174.7, 134.7, 81.5, 72.4, 67.3, 57.6, 54.0, 46.4, 37.3, and 20.4.

4.2.2 | 7b crosslinked resin

 $v_{\rm max}$ (KBr, cm⁻¹): 3468, 2948, 2793, 2472, 1730, and 1623 cm⁻¹; TGA: $T_{\rm D10}$ 177 °C (prepared in bulk), 171 °C (prepared in DMF solution); solid state ¹³C NMR (100 MHz): 174.4, 135.9, 82.3, 71.7, 66.8, 58.8, 44.7, 38.3, 36.3, 26.3, and 20.3.

4.2.3 | 7c crosslinked resin

 $v_{\rm max}$ (KBr, cm⁻¹): 3468, 2920, 2865, 1730, and 1659 cm⁻¹ TGA: $T_{\rm D10}$ 134 °C; solid state ¹³C NMR (100 MHz): 173.6, 78.4, 75.4, 72.9, 66.5, 44.1, 41.5, 27.2, 23.4, 17.9, and 13.5.

4.2.4 | 7d crosslinked resin

 v_{max} (KBr, cm⁻¹): 3484, 2960 and 1728 cm⁻¹; TGA: T_{D90} 282 °C; solid state ¹³C NMR (100 MHz): 174.3, 74.2, 66.4, 45.1, 41.3, 37.3, 27.9, 22.7, 18.6, and 12.9.

ORCID

Thomas J. Farmer ^b https://orcid.org/0000-0002-1039-7684

Michael North 🗅 https://orcid.org/0000-0002-6668-5503

REFERENCES

- [1] https://www.european-bioplastics.org/market/. Accessed 5 August 2022.
- [2] R. Geyer, J. R. Jambeck, K. L. Law, Sci. Adv. 2017, 3, e1700782.
- [3] (a)M. Eriksen, L. C. M. Lebreton, H. S. Carson, M. Thiel, C. J. Moore, J. C. Borerro, F. Galgani, P. G. Ryan, J. Reisser, *PLoS*

One **2014**, 9, e111913. (b) E. van Sebille, C. Wilcox, L. Lebreton, N. Maximenko, B. D. Hardesty, J. A. van Franeker, M. Eriksen, D. Siegel, F. Galgani, K. L. Law, *Environ. Res. Lett.* **2015**, *10*, 124006. (c) J. R. Jambeck, R. Geyer, C. Wilcox, T. R. Siegler, M. Perryman, A. Andrady, R. Narayan, K. L. Law, *Science* **2015**, *347*, 768.

- [4] (a) R. A. Sheldon, M. Norton, *Green Chem.* 2020, 22, 6310.
 (b) J.-P. Lange, *Energy Environ. Sci.* 2021, 14, 4358. (c) S. A. Backer, L. Leal, *Acc. Chem. Res.* 2022, 55, 2011.
- [5] (a) M. Vert, Biomacromolecules 2005, 6, 538. (b) G. X. De Hoe, T. Şucu, M. P. Shaver, Acc. Chem. Res. 2022, 55, 1514. (c) R. Yang, G. Xu, B. Dong, X. Guo, Q. Wang, ACS Sustain. Chem. Eng. 2022, 10, 9860. (d) Y. Liu, Z. Yu, B. Wang, P. Li, J. Zhu, S. Ma, Green Chem. 2022, 24, 5691.
- [6] J. H. Park, J. Y. Jeon, J. J. Lee, Y. Jang, J. K. Varghese, B. Y. Lee, *Macromolecules* 2013, 46, 3301.
- [7] T. J. Farmer, R. L. Castle, J. H. Clark, D. J. Macquarrie, Int. J. Mol. Sci. 2015, 16, 14912.
- [8] (a)S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini, C. K. Williams, *Chem. Commun.* 2015, *51*, 6459. (b) J. M. Longo, M. J. Sanford, G. W. Coates, *Chem. Rev.* 2016, *116*, 15167. (c) D. R. G. Printz, B. Jacques, S. Messaoudi, F. Dumas, S. Dagorne, F. Le Bideau, *Polym. Chem.* 2021, *12*, 2932. (d) X. Liang, F. Tan, Y. Zhu, *Front. Chem.* 2021, *9*, 647245. (e) A. J. Plajer, C. K. Williams, *Angew. Chem. Int. Ed.* 2022, *61*, e202104495. (f) W. T. Diment, W. Lindeboom, F. Fiorentini, A. C. Deacy, C. K. Williams, *Acc. Chem. Res.* 2022, *55*, 1997.
- [9] B. Liu, J. Chen, N. Liu, H. Ding, X. Wu, B. Dai, I. Kim, Green Chem. 2020, 22, 5742.
- [10] J. M. Longo, A. M. DiCiccio, G. W. Coates, J. Am. Chem. Soc. 2014, 136, 15897.
- [11] A. M. DiCiccio, G. W. Coates, J. Am. Chem. Soc. 2011, 133, 10724.
- [12] J. Liu, Y.-Y. Bao, Y. Liu, W.-M. Ren, X.-B. Lu, Polym. Chem. 2013, 4, 1439.
- [13] A. Takasu, M. Ito, Y. Inai, T. Hirabayashi, Y. Nishimura, *Polym. J.* **1999**, *31*, 961.
- [14] (a) C. Robert, F. de Montigny, C. M. Thomas, *Nat. Commun.* **2011**, *2*, 586. (b) N. J. Van Zee, M. J. Sanford, G. W. Coates, *J. Am. Chem. Soc.* **2016**, *138*, 2755.
- [15] (a) E. H. Nejad, C. G. W. van Melis, T. J. Vermeer, C. E. Koning, R. Duchateau, *Macromolecules* 2012, 45, 1770.
 (b) J. Y. Jeon, S. C. Eo, J. K. Varghese, B. Y. Lee, *Beilstein J. Org. Chem.* 2014, 10, 1787.
- [16] S. Huijser, E. Hosseini Nejad, R. Sablong, C. de Jong, C. E. Koning, R. Duchateau, *Macromolecules* 2011, 44, 1132.
- [17] (a) E. H. Nejad, A. Paoniasari, C. G. W. van Melis, C. E. Koning, R. Duchateau, *Macromolecules* 2013, 46, 631. (b) M. Proverbio, N. G. Galotto, S. Losio, I. Tritto, L. Boggioni, *Polymers* 2019, 11, 1222.
- [18] R. Mundil, Z. Hošťálek, I. Šeděnková, J. Merna, Macromol. Res. 2015, 23, 161.
- [19] L. Lin, J. Liang, Y. Xu, S. Wang, M. Xiao, L. Sun, Y. Meng, *Green Chem.* 2019, 21, 2469.
- [20] (a) B. Neises, W. Steglich, Angew. Chem. Int. Ed. 1978, 17, 522.
 (b) N. L. Benoiton, Chemistry of Peptide Synthesis, CRC Press, Boca Raton 2016.
- [21] B. Han, L. Zhang, B. Liu, X. Dong, I. Kim, Z. Duan, P. Theato, *Macromolecules* 2015, 48, 3431.
- [22] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. Ed. 2007, 46, 4434.

- [23] M. Jiang, J. Ma, M. Wu, R. Liu, L. Liang, F. Xin, W. Zhang, H. Jia, W. Dong, *Bioresour. Technol.* 2017, 245, 1710.
- [24] M. Zhao, X. Lu, H. Zong, J. Li, B. Zhuge, *Biotechnol. Lett.* 2018, 40, 455.
- [25] J. H. Crowell Production of itaconic and citraconic anhydrides. US2258947, 1941.
- [26] (a) A. M. DiCiccio, J. M. Longo, G. G. Rodriguez-Calero, G. W. Coates, J. Am. Chem. Soc. 2016, 138, 7107. (b) B. Zhang, H. Li, H. Luo, J. Zhao, Eur. Polym. J. 2020, 134, 109820.
- [27] M. Bernasconi, M.-A. Muller, A. Pfaltz, Am. Ethnol. 2014, 126, 5489.
- [28] I. Schoon, M. Kluge, S. Eschig, T. Robert, Polymer 2017, 9, 693.
- [29] R. Greco, L. Nicolais, Polymer 1976, 17, 1049.
- [30] (a) R. C. Jeske, A. M. DiCiccio, G. W. Coates, J. Am. Chem. Soc. 2007, 129, 11330. (b) K. Bester, A. Bukowska, B. Myśliwiec, K. Hus, D. Tomczyk, P. Urbaniak, W. Bukowski, Polym. Chem. 2018, 9, 2147.
- [31] C. Hoffmann, M. C. Stuparu, A. Daugaard, A. Khan, J. Polym. Sci., Part A: Polym. Chem. 2015, 53, 745.
- [32] (a) S. Lakshmi, A. Jayakrishnan, *Biomaterials* 2002, 23, 4855. (b) N. R. James, A. Jayakrishnan, *Biomaterials* 2003, 24, 2205.
- [33] G. J. Noordzij, Y. J. G. van den Boomen, C. Gilbert, D. J. P. van Elk, M. Roy, C. H. R. M. Wilsens, S. Rastogi, *Polym. Chem.* **2019**, *10*, 4049.

- [34] D. M. Lynn, R. Langer, J. Am. Chem. Soc. 2000, 122, 10761.
- [35] D. M. Day, T. J. Farmer, J. Sherwood, J. H. Clark, *Tetrahedron* 2022, 121, 132921. https://doi.org/10.1016/j.tet.2022.132921
- [36] V. V. Annenkov, S. V. Patwardhan, D. Belton, E. N. Danilovtseva, C. C. Perry, *Chem. Commun.* 2006, 1521.
- [37] C. M. Yakacki, M. Saed, D. P. Nair, T. Gong, S. M. Reed, C. N. Bowman, *RSC Adv.* 2015, *5*, 18997.
- [38] (a) D. Rutherford, D. A. Atwood, Organometallics 1996, 15, 4417. (b) R. L. Paddock, S. T. Nguyen, J. Am. Chem. Soc. 2001, 123, 11498. (c) D. J. Darensbourg, R. M. Mackiewicz, J. L. Rodgers, C. C. Fang, D. R. Billodeaux, J. H. Reibenspies, Inorg. Chem. 2004, 43, 6024.

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

How to cite this article: M. N. D. Haslewood, T. J. Farmer, M. North, *J. Polym. Sci.* **2022**, 1. https://doi.org/10.1002/pol.20220552