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Semi-Aromatic Polyesters derived from Renewable Terpene Oxides with High Glass Transitions

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ABSTRACT: The formation of bio-derived materials is gaining momentum in academic and industrial laboratories, though the use of terpene oxides as renewable monomers for the preparation of bio-based polymers yet remains limited. In order to advance the impact of such monomers, we have investigated the use of terpene derived epoxides (limonene oxide, carene oxide, limonene dioxide and menthene oxide) for the ring-opening copolymerization (ROCOP) in the presence of various aromatic anhydrides. These copolymerization reactions were mostly performed under mild reaction conditions (65°C, low loading of catalyst: 0.50 mol%) using a binary catalyst comprising of a Fe(III) based aminotriphenolate complex and PPNCI (bis(triphenylphosphine)iminium chloride) providing partially bio-based semi-aromatic polyesters with molecular weights of up to 25 Kg/mol ($\bar{D} = 1.54$) and glass transitions spanning a wide range from 59 to 243 °C. The copolymerization reactions proceed with excellent selectivity towards fully alternating polyesters ($\geq 98\%$ ester bonds) with modular thermal properties that depend on the nature of the terpene oxide used, and are potentially useful towards the development of new coating and thermoset materials.

INTRODUCTION

Synthetic polymers are essential for the production of a range of consumer-based products that focus on improving the quality of life. Due to an increasing demand to prepare such polymers in a sustainable fashion and to make use of renewable monomers derived from biomass,¹⁻⁴ there has been an upsurge in the development of partially to fully biodegradable polymers.⁵⁻¹² Such biobased macromolecules represent more benign alternatives for conventional polymers that for the larger part are prepared from petroleum based resources.¹³⁻¹⁵ In the context of biopolymer synthesis, terpene compounds have been frequently considered as functional monomers towards the construction of a variety of polymer structures including polyterpenes¹⁶⁻¹⁹ and polycarbonates.²⁰⁻²⁷ However, examples of polyesters derived from terpene based monomers remain scarce,²⁸⁻³⁴ despite their abundance and structural diversity and potential for post-modification and curing.

The ring-opening polymerization (ROP) of cyclic esters in the presence of suitable organic or metal-based initiators produces polyesters such as poly(lactide), and is an attractive and easy to control the polymerization process.³⁵⁻³⁸ However, the diversity in cyclic ester structures and limitations in functional group presence in these polyesters may limit the properties that can be attained through the use of these monomers. Therefore, complementary polyester preparation strategies offer a way to produce polymers with a wider range of properties modulated by the nature of the monomers, and ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides³⁹⁻⁴¹ has been recognized as a highly versatile route to further extend the (thermal) properties of polyesters. In particular, the synthesis of aliphatic polyesters prepared through the perfectly alternating ROCOP of aliphatic cyclic esters and epoxides represents an active field of research. Early work in this area showed the potential of ROCOP when using Al(III) centered

porphyrins as catalysts,³⁹ whereas a major breakthrough in the ROCOP was not noted until the use of a β -diiminate Zn-catalyst was reported.²⁸ Apart from this seminal report, other catalysts have also been reported in this context as highly efficient mediators of ROCOP using a variety of cyclic anhydrides and epoxides.⁴²⁻⁴⁵ The thermal properties of aliphatic polyesters can be easily regulated through ROCOP and this approach can provide macromolecular structures with long side chains and/or extremely flexible backbones providing consequently low T_g values (typically below 0°C) with potential towards the development of new thermoplastic elastomers.^{46,47} Alternatively, the development of higher T_g , purely aliphatic polyester variants with values beyond 100°C still remains in its infancy. Important progress was recently reported by Coates and coworkers,²⁸ who used a rigid terpene-based tricyclic anhydride and propylene oxide (PO) to yield a polyester (M_n = 55 kDa) with a T_g of 109°C. Analogous to the approach from Coates, Liu and coworkers considered organocatalytic ROCOP of a norbornene-based tricyclic anhydride monomer and cyclohexene oxide (CHO) giving also high T_g (up to 130°C) polyesters though with significantly lower M_n values.⁴⁵ The highest T_g 's for aliphatic polyesters (up to 184°C) derived from a series of partially renewable cyclic anhydrides combined with PO or CHO under Al(III) or Fe(III) catalysis were reported by Coates and Kleij, showing the importance of selecting more rigid monomer combinations to further extend and modify the thermal properties.³¹

Semi-aromatic polyesters, *i.e.* polyesters constructed from one aromatic monomer, also have good potential to produce polymers with higher T_g values.⁴⁸⁻⁵¹ In this context, phthalic anhydride (PA) is the most commonly used monomer and when this monomer is copolymerized in the presence of (substituted) cyclohexene oxides⁴⁷ or cyclohexadiene oxide⁵² it produces polyesters with T_g values of 146°C (M_n = 13.2 kDa) and 128°C (M_n = 7.5 kDa), respectively. Inspired by these results and our ongoing interest in using renewable terpene feed stocks,^{23,26,53} considered the

ROCOP of PA and various terpene oxides as a useful approach towards semi-aromatic polyesters with modular thermal properties by a proper selection of the combination of monomers, catalyst and reaction conditions. As far as we know, there are only very few successful examples of ROCOP between (aromatic) cyclic anhydrides and terpene oxides.²⁸⁻³⁴ Thomas *et al.* reported the use of limonene oxide (LO) and pinene oxide (PiO) monomers in the preparation of aliphatic polyesters. This tandem approach involved *in situ* cyclic anhydride synthesis from a dicarboxylic acid precursor and a dicarbonate reagent, followed by a ROCOP with LO or PiO at 100°C under metal-salen catalysis.²⁹ Duchateau and coworkers also used M(salen) catalysts (M = Al, Cr, Mn and Co) to mediate the ROCOP of PA and LO at 130°C under neat conditions. The polyesters produced this way had M_n values up to 9.7 kg/mol ($\bar{D} = 1.4$), and they further reported a moderately high T_g of 82°C for a polyester having a molecular weight of 7.2 kg/mol.³⁰ Therefore, further expansion of the potential of terpene oxide monomers in the synthesis of high T_g semiaromatic polyesters is still a challenging but inspiring objective in the realm of biobased polymer development.

Herein we present an Fe(III) based catalyst⁵⁴⁻⁵⁶ derived from an aminotriphenolate ligand that, in the presence of a suitable initiator, mediates the ROCOP of various terpene based monomers towards the preparation of semi-aromatic polyesters under mild reaction conditions providing molecular weights of up to an appreciable 25 kg/mol and allowing for a T_g modulation between 59 and 243°C.

RESULTS AND DISCUSSION

ROCOP of PA and LO using the Binary Catalysts Derived from (1) or (2). Based on our previous experience and success with Fe-centered aminotriphenolate complexes in the activation of sterically more demanding epoxide substrates,^{57,58} we selected Fe-complex **1** (Fe^{Me}) as epoxide activator and bis(triphenylphosphine)iminium chloride (PPNCl) as initiator⁵⁹ of the ROCOP of PA and the trisubstituted monomer limonene oxide (commercial *cis/trans*-LO, *cis/trans* = 40:60) as benchmark reaction. For comparative reasons, we also employed Al(III) complex **2** and DMAP (4-dimethylamino-pyridine) as epoxide activator and initiator, respectively. The only known example of such a sterically more challenging copolymerization reaction was reported by Duchateau *et al.*³⁰ who initially used a Cr(III)saphen/DMAP catalyst operated at 130°C. We envisioned that the conformationally more flexible complexes Fe^{Me} (**1**) and Al^{Me} (**2**) should be able to mediate the alternating copolymerization of LO and PA under milder reaction conditions.

Thus, initial trials were carried out at a relatively low reaction temperature of 65°C in various solvents (Table 1; entries 1–6) using first Fe^{Me} (**1**) and DMAP at low loading (0.50 mol%). Fortunately, the copolymerization of LO and PA proceeded though relatively slow and provided a high quality of poly(PA-*alt*-LO) under excellent control ($\geq 98\%$ ester bonds) and with reasonable molecular weight and low dispersity ($M_n = 10.7$ kg/mol; $\bar{D} = 1.24$). Interestingly, the isolated polymer from entry 1 exhibited a high T_g value of 135°C which is significantly higher than the value reported by Duchateau and coworkers (82°C).³⁰ The use of PPNCl as initiator (entry 2) gave fairly similar results in terms of M_n , $\bar{D}$ and T_g data, but proved to be significantly faster. Then other solvents (entries 3–6; DCM, CH_3CN , DMF and toluene) were probed but these copolymerization attempts all gave poorer results.

Table 1. ROCOP of LO and PA using Fe^{Me} (**1**) or Al^{Me} (**2**) and PPNCI or DMAP as Initiators.^a

Nu stands for nucleophile.

Entry	[M] (mol%)	[Nu] (mol%)	Solv.	t (h)	Conv. (%) ^b	M_n^c (kg/mol)	$\bar{D}^{c,d}$	T_g ($^{\circ}\text{C}$) ^e
1	1 , 0.50	DMAP, 0.50	THF	48	92	10.7	1.24	135
2	1 , 0.50	PPNCI, 0.50	THF	24	84	10.5	1.24	131
3	1 , 0.50	PPNCI, 0.50	DCM	24	49	5.6	1.39	110
4	1 , 0.50	PPNCI, 0.50	Tol	24	46	5.6	1.28	111
5 ^f	1 , 0.50	PPNCI, 0.50	DMF	24	10	—	—	—
6 ^f	1 , 0.50	PPNCI, 0.50	ACN	24	25	—	—	—
7 ^g	1 , 0.50	PPNCI, 0.50	—	24	>99	9.5	1.21	115
8 ^h	1 , 0.50	PPNCI, 0.50	—	24	>99	5.5	1.24	95
9	2 , 0.50	DMAP, 0.50	THF	48	87	4.3	1.24	104
10	2 , 0.50	PPNCI, 0.50	THF	48	71	5.5	1.21	124
11	2 , 0.25	DMAP, 0.25	THF	48	62	8.0	1.24	120
12	2 , 0.25	PPNCI, 0.25	THF	48	46	6.9	1.26	124
13 ^g	1 , 0.50	—	—	24	0	—	—	—
14 ^{f,g}	—	PPNCI, 0.50	—	24	26	—	—	—
15	1 , 0.50	—	THF	24	0	—	—	—

16 ^f	–	PPNCl, 0.50	THF	24	8	–	–	–
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^aReaction conditions: 1.5 mmol PA, solvent (0.50 mL), T = 65°C, [PA]:[LO] = 1:1.1. ^bConversion of PA determined by ¹H NMR (CDCl₃); selectivity for the alternating polymer ≥ 98%, regioselectivity not determined. ^cDetermined by GPC in THF (30°C) using polystyrene standards for calibration. ^d $\bar{D} = M_w/M_n$. ^eDetermined by differential scanning calorimetry (DSC), the data refer to the second heating cycle. ^fPolymer not isolated. ^g[PA]:[LO] = 1:2. ^h[PA]:[LO] = 1:5.

Next we focused on further improving the formation of poly(PA-*alt*-LO) by performing the reactions under solvent-free conditions though using a larger excess of LO (entries 7 and 8; 2 and 5 equiv, respectively). Particularly, the use of 2 equiv of LO (entry 7) gave full conversion of the PA in 24 h and the molecular weight and dispersity were comparable to the ones obtained in the solution phase process (entry 2) despite the lower T_g value (115°C) measured. Alternatively, the use of **Al^{Me}** (**2**) as catalyst for the solution phase copolymerization leading to poly(PA-*alt*-LO) (entries 9–12) showed somewhat lower PA conversions and inferior molecular weights compared to the use of **Fe^{Me}** (**1**), and therefore further studies were conducted using the latter complex. Notably, the presence of **1** was required to facilitate the activation of LO for nucleophilic ring-opening by PPNCl, and as a consequence a much faster propagation was noted (*cf.*, entries 14 and 16 versus 2 and 7), whereas the use of only **1** proved to be unproductive as expected (entries 13 and 15).

ROCOP of various Terpene Oxides and PA using the Binary Catalyst Fe^{Me}/PPNCl. The use of various terpene oxides including *cis/trans*-LO, *cis*-LO, carene oxide (CAO), methene oxide (MEO) and the bifunctional limonene dioxide (LDO) was examined in the ROCOP using PA as the cyclic anhydride substrate. For comparative reasons, some of the best results obtained with the *cis/trans*-LO substrate (Table 1) are listed here as well (Table 2, entries 1 and 2). While the use of *cis/trans* limonene oxide (LO) under attractive conditions (65°C, 0.50 mol% of complex **1** and PPNCl) provided appreciable molecular weight poly(PA-*alt*-LO), the ROCOP of *cis*-LO (entries

3 and 4) and PA gave a superior grade polyester with M_n values of up to 16.4 kg/mol. As observed throughout the copolymerization reactions, the solution phase experiments gave consistently better results in terms of polymer quality. Interestingly, the use of the diastereo-isomerically pure *cis*-LO monomer resulted in a polyester with an improved and high T_g value of 141°C (entry 3). The promising results obtained using limonene oxide as a renewable terpene-based monomer in polyester synthesis prompted us to consider other terpene oxide monomers including those based on carene (CAO) and menthene (MEO). Apart from these two monomers, we also selected

Table 2. ROCOP of various Terpene Oxides and PA using Fe^{Me} (**1**)/PPNCl as Binary Catalyst.^a

Entry	Sub.	[1]/PPNCl (mol%)	Solv.	t (h)	Conv. (%) ^b	M_n^c (kg/mol)	$\bar{D}^{c,d}$	T_d^{10} (°C) ^e	T_g (°C) ^f
1	LO	0.50, 0.50	THF	24	84	10.5	1.24	255	131
2 ^g	LO	0.50, 0.50	—	24	>99	9.5	1.21	—	115
3	<i>cis</i> -LO	0.50, 0.50	THF	24	>99	16.4	1.33	258	141
4 ^g	<i>cis</i> -LO	0.50, 0.50	—	24	>99	9.2	1.44	—	129
5	CHDO	0.50, 0.50	THF	40	85	24.9	1.54	309	132
6	CHDO	0.50, 0.50	—	48	>99	19.6	1.42	—	105
7	CAO	0.50, 0.50	THF	100	79	3.7	1.39	210	130
8 ^{g,h}	CAO	0.50, 0.50	—	48	89	3.3	1.52	—	112

9	MEO	0.50, 0.50	THF	24	56	3.2	1.24	–	155
10 ^g	MEO	0.50, 0.50	–	24	75	5.1	1.28	–	161
11 ^g	MEO	0.30, 0.30	–	72	75	12.7	1.20	297	165
12 ⁱ	LDO	0.50, 0.50	THF	24	33	8.7	1.94	287	59
13 ^{g,i}	LDO	0.50, 0.50	–	24	52	6.7	2.41	–	53

^aReaction conditions: 1.5 mmol PA, solvent (0.50 mL), T = 65°C unless stated otherwise, [PA]:[Sub] = 1:1.1. ^bConversion of PA determined by ¹H NMR (CDCl₃); selectivity for the alternating polymer ≥ 98%, regioselectivity not determined. ^cDetermined by GPC in THF (30°C) using polystyrene standards for calibration. ^d $\bar{D} = M_w/M_n$. ^eFrom thermogravimetric analysis, data refer to T_d^{10} values at 10% wt loss. ^fDetermined by differential scanning calorimetry (DSC), the data refer to the second heating cycle. ^g[PA]:[epox] = 1:2. ^hReaction performed at 95°C. ⁱReaction performed at 45°C.

cyclohexadiene oxide (CHDO; a renewable, terpene-like monomer that can be derived from cyclohexadiene, a byproduct from oleochemical olefin metathesis),⁵² and the bisepoxide from limonene (LDO).^{60,61} The most prominent results were obtained in the ROCOP using CHDO or MEO as monomers (entries 5–6 and 10–11, respectively). In the case of CHDO, high molecular weight poly(PA-*alt*-CHDO) was obtained up to 25 kg/mol ($\bar{D} = 1.54$) in the solution phase polymerization, though the reaction times required for high monomer (PA) conversion were typically longer (40–48 h; entries 5 and 6) compared to the copolymerizations carried out with LO or *cis*-LO. The highest T_g value (132°C) for poly(PA-*alt*-CHDO) is slightly above the value reported by Williams, Meier and coworkers ($T_g = 128^\circ\text{C}$, $M_n = 7.5$ kg/mol, $\bar{D} = 1.17$)⁵² despite the much higher molecular weights produced by our binary catalyst system **1**/PPNCl.

The conversion of the bulky monomer carene oxide (CAO) was a challenge and long reaction times were needed for high PA conversion in solution phase (entry 7). Though a shorter reaction time was required when applying bulk copolymerization (entry 8) a higher reaction temperature was needed (95°C). The solution phase experiment provided slightly better quality poly(PA-*alt*-CAO) ($M_n = 3.7$ kg/mol, $\bar{D} = 1.39$) with a relatively high T_g value of 130°C. The use of menthene

oxide (MEO) in the ROCOP process provided poly(PA-*alt*-MEO) grades with molecular weights of up to 12.7 kg/mol (entries 9–11) and to our delight a very high T_g of 165°C (see Figure 1, **b**). As far as we know, this is the highest T_g value reported for a semi-aromatic polyester based on PA. The bifunctional monomer limonene dioxide (LDO; entries 12 and 13) was also copolymerized with PA to afford poly(PA-*alt*-LDO) at low reaction temperature (45°C): at higher reaction temperatures insoluble (presumably highly cross-linked materials) were produced. Though reasonable molecular weights of 6.7 and 8.7 kg/mol were attained for poly(PA-*alt*-LDO), the polydispersities for these copolymers were quite high ($\bar{D} = 1.9$ –2.4) which can be attributed to a low degree of control over the site-specific alternating copolymerization with PA in this bifunctional monomer. Importantly, all polyesters described in Table 2 exhibited decomposition onsets (T_d^{10}) typically 110–120°C higher than their respective T_g values which should allow to easily process these polyesters in coating preparations.

NMR Analysis of Polyesters. The majority of the polyester products from Table 2 were isolated as compounds with clean and defined NMR features. The polymers based on LO and *cis*-LO only showed subtle differences in the NMR spectra, but essentially these polymers were free of any detectable ether linkages (see Figure 2, **a+b**). The polyester derived from CHDO (Figure 2, **c**) also showed a well-resolved NMR spectrum in line with a high degree of control over the ROCOP process exerted by the binary catalysts **1**/PPNCl. The much lower molecular weight obtained for poly(PA-*alt*-CAO) (Figure 2, **d**) upon coupling of CAO with PA allows for easy detection of end-groups around 5.0 ppm. The case of MEO/PA copolymerization (Figure 2, **e**) shows primarily two sets of signals in the region for the protons indicated as **1** and **2** that are situated next to the ester linkages. The MEO was derived from a single enantiomer of menthene (menthene was obtained from pure (-)-menthol) and upon epoxidation two diastereoisomers of

MEO are formed in an approximate 3:1 ratio (see the SI). This feature is clearly maintained in the repeat units of the poly(PA-*alt*-MEO) and the observed broadening of the peaks in the region 5.0–5.6 ppm is a result of protons **1** and **2** being inequivalent due to the asymmetric nature of the menthene backbone. Lastly, the NMR features of the polyester prepared from the bifunctional monomer LDO reveal a relatively ill-defined polymer structure with a significant amount of epoxide groups (*cf.*, Figure 2, **f**: 3.0–3.6 ppm) still remaining in the isolated poly(PA-*alt*-LDO).

Figure 1. Selected regions of the DSC traces of (a) poly(PA-*alt*-LO), entry 1 Table 2, (b) poly(PA-*alt*-MEO), entry 11 Table 2, (c) poly(NA-*alt*-CHO), entry 1 Table 3, and (d) poly(NA-*alt*-LO), entry 5 Table 3. In all cases, the traces refer to the second heating cycle. For full details see the SI.

Apparently, when the copolymerization of LDO and PA is carried out at 45°C using the binary system **1**/PPNCl both epoxide groups are involved in “at random” ester formation reactions and no site-specific selectivity can be induced. At a higher reaction temperature we were only able to

isolate insoluble material, and our interpretation is that this observation is related to a high(er) degree of uncontrollable crosslinking in the polyester structure.

ROCOP of CHO and LO with 1,8-Naphthalic Anhydride using the Binary Catalyst $\text{Fe}^{\text{Me}}/\text{PPNCl}$. Having successfully developed high T_g semi-aromatic polyesters based on various

Figure 2. ^1H NMR traces (CDCl_3) of the isolated polyesters reported in Table 2 based on PA and (a) *cis/trans* limonene oxide (LO); (b) *cis* limonene oxide (*cis*-LO); (c) cyclohexadiene oxide (CHDO); (d) carene oxide (CAO); (e) menthene oxide (MEO) and (f) limonene dioxide (LDO)

with remaining epoxide groups indicated. Some characteristic peaks have been highlighted, for more details see the SI. The asterisks denote solvent impurities. Note that there are multiple isomeric repeat units possible for all polymers (except under c); likely their resonances are overlapping and for simplicity only one type of unit is drawn.

Table 3. ROCOP of various CHO or *cis/trans*-LO and 1,8-Naphthalic Anhydride (NA) using **Fe^{Me}** (**1**)/PPNCl as Binary Catalyst.^a

Entry	Sub.	Solv.	T (°C)	t (h)	Conv. (%) ^b	M_n^c (kg/mol)	$\bar{D}^{c,d}$	T_d^{10} (°C) ^e	T_g (°C) ^f
1	CHO	THF	65	72	79	11.4	1.25	330	208
2	CHO	DCM	65	72	>99	2.5	2.35	–	182
3	CHO	Tol	65	72	31	2.3	1.81	–	190
4 ^g	CHO	–	95	72	>99	6.9	1.71	–	182
5	LO	THF	65	72	50	2.2	1.36	268	243
6 ^g	LO	–	95	72	50	1.6	1.52	–	227

^aReaction conditions: 1.5 mmol NA, solvent (0.50 mL), [NA]:[Sub] = 1:1.1, [1]: 0.50 mol%, PPNCl: 0.50 mol%. ^bConversion of NA determined by ¹H NMR (CDCl₃); selectivity for the alternating polymer ≥ 98%, regioselectivity not determined. ^cDetermined by GPC in THF (30°C) using polystyrene standards for calibration. ^d $\bar{D} = M_w/M_n$. ^eFrom thermogravimetric analysis, data refer to T_d^{10} values at 10% wt loss. ^fDetermined by differential scanning calorimetry (DSC), the data refer to the second heating cycle. ^g[NA]:[LO] = 1:2.

terpene monomers, we then selected a more rigid and commercially available cyclic anhydride (1,8-naphthalic anhydride, NA) and investigated the ROCOP with both CHO and LO (Table 3). In principle, the more rigid character of NA should provide increased rigidity in alternating polyesters, and first copolymerization experiments were conducted with the more reactive monomer CHO (entries 1–4) under catalysis of the binary system **1**/PPNCl at 65°C. The use of a solvent in these copolymerization experiments was warranted due to the rather insoluble nature of the NA. The solution phase reactions carried out with CHO and NA were performed in THF, DCM and toluene and compared with the bulk polymerization at an elevated reaction temperature (entry 4, 95°C). As may be expected for the coupling of the sterically more crowded anhydride NA, in all cases the copolymerization was comparatively slow and longer reaction times were needed for high NA conversion. Under these conditions, the use of toluene was not beneficial as only a rather low NA conversion of 31% was achieved in 72 h. The use of DCM facilitated much higher NA conversion but the polyester quality (entry 2; $M_n = 2.5$ kg/mol, $D = 2.35$) was significantly lower than observed when THF was used as solvent (entry 1; $M_n = 11.4$ kg/mol, $D = 1.25$). Remarkably, the glass transitions exhibited by these poly(NA-*alt*-CHO) were high and the T_g 's of these polymers reached up to 208°C (Figure 1, c). Despite the fact that the bulk copolymerization (entry 4) provided quantitative NA conversion, the polymer properties of the poly(NA-*alt*-CHO) were inferior to the ones from the solution phase ROCOP of CHO and NA carried out in THF. Next, the use of LO was probed and similar reactions conditions as reported in entries 1 and 4 were taken as a starting point towards the preparation of poly(NA-*alt*-LO) (*cf.*, entries 5 and 6). As opposed to the use of CHO, the lower reactive LO monomer provides only moderate NA conversion of around 50% in 72 h, and low molecular weights of up to 2.2 kg/mol with a calculated degree of

polymerization (DP) of only 7. However, the analysis of the thermal behavior of these oligomeric macromolecules reveals a high level of rigidity as testified by their T_g values of up to 243°C (see Figure 1, **d**). Thus, by a proper selection of terpene oxide and anhydride monomers the glass transitions of semi-aromatic polyesters can be tuned over a wide range spanning more than 100°C.

CONCLUSION

In summary, we present here an effective catalyst based on Fe(III) complex **1** that mediates the ROCOP of various renewable/terpene oxides and cyclic anhydrides giving access to semi-aromatic polyesters with molecular weights of up to 25 kg/mol, low polydispersities and typically excellent chemo-selectivity control with exclusive ester bond formation ($\geq 98\%$ ester bonds). Moreover, the polyesters formed from limonene oxide, cyclohexadiene oxide and menthene oxide show promise towards the formation of highly rigid phthalate based polymers with T_g 's of up to 165°C and T_d^{10} values at least 110–120°C above the determined glass transitions. The use of the highly rigid monomer naphthalic anhydride further allowed for tuning the glass transition behavior of these partially renewable polyesters to values far beyond 200°C. The used ROCOP catalyst is a rare case of a system that can effectively produce terpene oxide based polyesters for which the T_g 's can be tuned over a wide and high temperature range. The thermal properties of the developed polyesters should be of interest towards the formation of di-block copolymers of potential importance in coating applications for a range of (new) applications.

EXPERIMENTAL SECTION

General Considerations. All water sensitive operations were carried out under nitrogen atmosphere using an Mbraun glovebox, standard vacuum-line and Schlenk techniques. Solvents

were purchased from Sigma-Aldrich (HPLC grade) and dried using an MBraun MBSPS800 purification system. All reagents were purchased from commercial suppliers (Aldrich and Acros) and used as received. FT-IR measurements were performed on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam-splitter at 4 cm^{-1} resolution. NMR spectra were recorded on a Bruker AV-400 spectrometer and referenced to the residual NMR solvent signals. Glass transition temperatures (T_g) were measured under an N_2 atmosphere using a Mettler Toledo equipped, model DSC822e. Samples were weighed into $40\text{ }\mu\text{L}$ aluminum crucibles and subjected to three heating cycles at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. Thermo-gravimetric analyses were recorded under a N_2 atmosphere using Mettler Toledo equipment (model TGA/SDTA851) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran at $40\text{ }^\circ\text{C}$ at a flow rate of $1\text{ mL}\cdot\text{min}^{-1}$. Samples were analyzed at a concentration of $3\text{ mg}\cdot\text{mL}^{-1}$ after filtration through a $0.45\text{ }\mu\text{m}$ pore-size membrane. The separation was carried out on three polystyrene/divinylbenzene columns from Agilent: PLgel $5\text{ }\mu\text{m}$ MIXED-C, $300\times 7.5\text{ mm}$. The setup (Viscotek TDA305) was equipped with a refractive index (RI) detector ($\lambda = 670\text{ nm}$). M_n , M_w and M_w/M_n ($\mathcal{D}$) were derived from the RI signal by a calibration curve based on polystyrene standards (PS from Polymer Standards Service) for the analysis of the polymers. GPC measurements for the polymers were performed by the Instituto de Ciencia y Tecnologia de Polímeros de Madrid. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) were performed by the Research Support Group at ICIQ on a BRUKER Autoflex spectrometer using dithranol as a matrix and CF_3COONa as an additive.

Reagents and Complexes. The anhydride substrates PA and NA are commercially available and were used after purification (recrystallization from hot chloroform) and dried under vacuum over 24 h . The terpene oxide precursors are commercially available. *Cis*-limonene oxide,⁶²

cyclohexene oxide⁶³ and carene oxide [(+)-(1*S*, 3*S*, 4*R*, 6*R*)-3,4-epoxy-3,7,7-trimethylbicyclo[4.1.0]heptane]⁶⁴ were prepared following literature procedures and purified by distillation from CaH₂. Menthene oxide (2-isopropyl-5-methyl-7-oxabicyclo[4.1.0]heptane)⁵³ was prepared following literature procedures from (-)-menthol and purified by distillation from CaH₂. LDO (1-methyl-4-(2-methyloxiran-2-yl)-7-oxabicyclo[4.1.0]heptane)^{60,61} was also prepared following literature procedures from the commercially *cis* and *trans* limonene oxide mixture and purified by distillation from CaH₂. Commercially available initiators bis(triphenylphosphine)iminium chloride, PPNCl, and 4-dimethylaminopyridine, DMAP, were purified by recrystallization from dichloromethane and dried under vacuum at 40°C over 24 h. The complexes **1**⁵⁷ and **2**⁶⁵ were prepared following previously reported procedures.

Procedure for the ROCOP Reactions. All reaction mixtures were prepared in a glove box under moisture-free conditions. The binary catalyst (metal complex and initiator) and 1.5 mmol of the corresponding anhydride were placed in an oven-dried 4 mL vial equipped with a magnetic stir bar. The appropriate amount of epoxide and solvent were added and the vial was sealed with a Teflon-lined cap. The reaction mixture was then removed from the glove box and placed in an aluminum heating block preheated at the desired reaction temperature. The reaction mixture was monitored by ¹H NMR spectroscopy. After the ROCOP reaction, the volatiles were removed under vacuum. The crude product was dissolved in a minimal amount of dichloromethane and precipitated with a solution of HCl (1 M) in methanol. This latter procedure was repeated three times and finally the polymer was washed with methanol (three times) and dried under vacuum.

ASSOCIATED CONTENT

Supporting Information. Further experimental details, spectra of isolated polymer samples (NMR and IR), and relevant GPC, MALDI-TOF-MS, DSC and TGA traces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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