

This document is confidential and is proprietary to the American Chemical Society and its authors. Do not copy or disclose without written permission. If you have received this item in error, notify the sender and delete all copies.

Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures

Journal:	<i>Macromolecules</i>
Manuscript ID	ma-2016-014256.R1
Manuscript Type:	Article
Date Submitted by the Author:	03-Aug-2016
Complete List of Authors:	Sanford, Maria; Cornell University, Chemistry and Chemical Biology Leticia Peña Carrodeguas, Leticia; Institute of Chemical Research of Catalonia (ICIQ), Van Zee, Nathan; Cornell University, Kleij, Arjan; Institute of Chemical Research of Catalonia (ICIQ), Research group Kleij Coates, Geoffrey; Cornell University, Chemistry and Chemical Biology; Cornell University, Chemistry and Chemical Biology

SCHOLARONE™
Manuscripts

"This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Macromolecules* 2016, 49, 6394-6400, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see DOI: 10.1021/acs.macromol.6b01425. This article may be used for non-commercial purposes in accordance with the ACS guidelines published at <http://pubs.acs.org/page/policy/articlesonrequest/index.html>."

1
2
3
4
5
6
7 Alternating Copolymerization of Propylene Oxide
8
9
10
11 and Cyclohexene Oxide with Tricyclic Anhydrides:
12
13
14
15 Access to Partially Renewable Aliphatic Polyesters
16
17
18
19
20 with High Glass Transition Temperatures
21
22
23
24

25 *Maria J. Sanford,[‡] Leticia Peña Carrodegua,[§] Nathan J. Van Zee,^{†,‡} Arjan W. Kleij,^{*,§} and*
26
27 *Geoffrey W. Coates^{*,‡}*
28
29
30

31 [‡]Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca,
32
33 NY 14853-1301, USA
34
35

36 [§]Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona,
37
38 Spain
39
40
41
42

43 ABSTRACT: Renewable, biodegradable polymers, such as aliphatic polyesters, based on
44 sustainable sources have attracted considerable interest as alternatives to petroleum based
45 polymers. One limiting factor in the development of aliphatic polyesters as replacements for
46
47 these materials has been their relatively low glass transition temperatures (T_g). For example,
48 commercially available poly(lactic acid) has a T_g of approximately 60 °C. Epoxide/anhydride
49
50 copolymerizations offer an alternative to the ring-opening polymerization of lactones for the
51
52 synthesis of aliphatic polyesters, and allow for tuning of polymer properties through two distinct
53
54
55
56
57
58
59
60

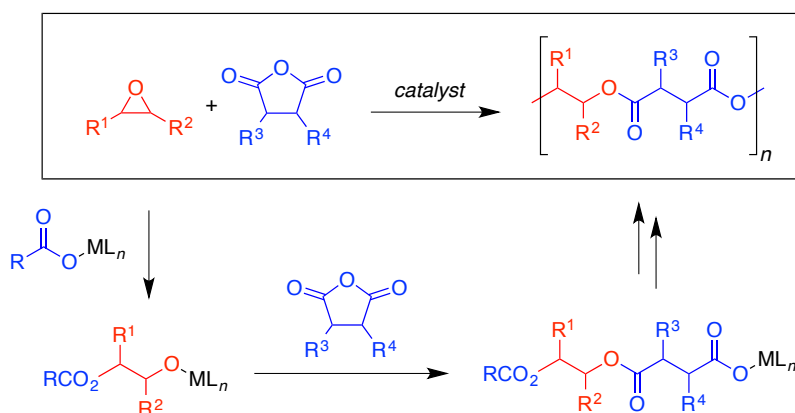
1
2
3 monomer sets. We synthesized six partially or fully renewable tricyclic anhydrides and
4
5 copolymerized them with propylene oxide (PO) and cyclohexene oxide (CHO). By varying both
6
7 the epoxide and the anhydride we were able to tune the T_g of the resulting polymers over a nearly
8
9 120 °C range from 66 °C to an exceptionally high 184 °C. Polymers produced with PO had a
10
11 lower range of T_g values (66–108 °C) and higher molecular weights up to 32.2 kDa, while those
12
13 produced with CHO had higher T_g values (124–184 °C) and lower molecular weights, showing
14
15 the profound influence of both monomer sets. To the best of our knowledge, these are the highest
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
 T_g values reported for entirely aliphatic polyesters.

As society has become more dependent on plastics, the sustainability of these materials has become an increasingly important issue. Polymers that are produced from sustainable feedstocks such as biomass and those that are biodegradable have attracted considerable interest as alternatives to fossil fuel-based polymers.¹ In particular, aliphatic polyesters are appealing because of their numerous renewable sources,^{1b,1d,2} facile hydrolytic degradation to benign products,^{2b,3} and general biocompatibility.⁴ These features have led to aliphatic polyesters being utilized in applications ranging from specialized biomedical devices to bulk packaging.^{4,5}

The most common route to produce aliphatic polyesters is the ring-opening polymerization (ROP) of lactones and lactide.⁶ Numerous initiators have been used for lactone polymerization, including organocatalysts, metal alkoxides, and various metal complexes.⁴ However, the ROP of lactones can be limited by detrimental side reactions such as transesterification, especially at high conversion. The resulting polymers also have a limited range of properties, because of the limited functional diversity of the substrate scope and lack of post-polymerization

functionalization on the resulting polyesters.^{4,6} There has been interest in developing higher T_g aliphatic polyesters, since commercially available poly(lactic acid) (PLA) has a relatively low T_g (approximately 60 °C). Efforts to improve the T_g of aliphatic polyesters have mainly focused on using polysaccharide derived diols,⁷ and lactide⁸ or mannitol⁹ derivatives. However, the resulting polymers either show modest improvements over PLA (T_g up to 68 °C),^{7a,9} or require long reaction times at low temperatures (-20 °C) to reach moderate conversion.⁸ An alternative synthetic route to aliphatic polyesters is the alternating copolymerization of epoxides and cyclic anhydrides (Scheme 1).⁶ The use of two monomers allows for more facile tuning of properties, and many of the resulting polyesters can be easily functionalized by post-polymerization modification.^{6,10} There is a diverse array of metal complexes reported to catalyze the copolymerization, including zinc,¹¹ magnesium,^{11d,11f,12} chromium,^{11f,13} cobalt,^{11f,13b,13d-f,13i,14} manganese,^{13b,13i,15} and aluminum^{13b,13e,13f,13i,16} complexes, including a wide range of salen- and porphyrin-type complexes which generally show markedly improved activity with the addition of a nucleophilic co-catalyst such as bis(triphenylphosphine)iminium chloride ([Ph₃P-N=PPh₃]Cl or [PPN]Cl).

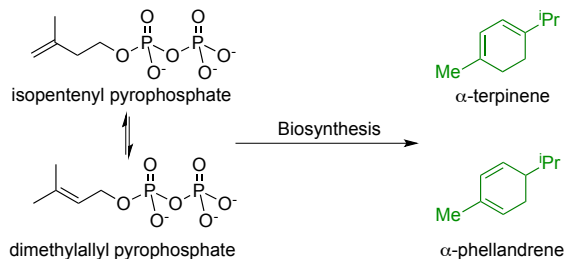
Scheme 1. Alternating copolymerization of epoxides and cyclic anhydrides, and simplified proposed reaction mechanism.



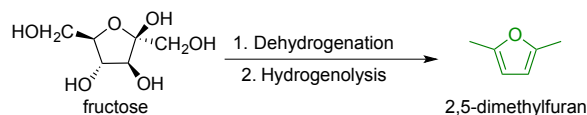
1
2
3 The Coates group has recently focused on the alternating copolymerization of epoxides and
4 tricyclic anhydrides with aluminum salen complexes.^{16c,16d} Tricyclic anhydrides are appealing
5 monomers that are easily synthesized via the Diels-Alder reaction. The wide range of
6 commercially available, inexpensive, biosourced dienes and dienophiles offers ample
7 opportunities for utilizing renewable feedstocks. Additionally, the rigid nature of the resulting
8 polymers yields materials with high glass transition temperatures (T_g). Recently, we reported the
9 chain-growth copolymerization of propylene oxide and a terpene based tricyclic anhydride,
10 which yielded a completely amorphous aliphatic polyester with a T_g of 109 °C.^{16c} Additionally,
11 transesterification and epimerization could be suppressed even at high conversion through
12 judicious choice of catalyst, the ratio of catalyst to cocatalyst, and the steric requirements of the
13 monomers.^{16c,16d} In addition to screening these (salen)AlCl catalysts for a wider range of
14 monomers, we were also interested in exploring a geometrically more flexible¹⁷ iron
15 aminotriphenolate complex because it has been shown to be active for copolymerization of
16 epoxides and CO₂,¹⁸ and iron complexes have previously been used in epoxide/anhydride
17 copolymerizations. Recently, Merna and coworkers reported the use of (salen)FeCl complexes
18 for the copolymerization of cyclohexene oxide and phthalic anhydride,¹⁹ and Nozaki reported
19 using an iron corrole complex for the alternating copolymerization of propylene oxide and
20 glutaric anhydride.^{15a} In general, iron complexes are of interest due to the high natural abundance
21 of iron and its low toxicity. Because of the potential uses of aliphatic polyesters in biomedical
22 applications, metal catalysts with low toxicity are of interest because of residual catalyst trapped
23 in the polymer. Herein, we report an expansion of our previous work to six anhydrides and two
24 epoxides to synthesize twelve partially renewable aliphatic polyesters with T_g values that are
25 tunable from 66 °C to 184 °C.
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Scheme 2. Synthesis of renewable precursors for tricyclic anhydrides.

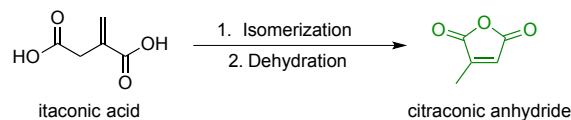
Terpenes: Naturally occurring feedstocks



2,5-Dimethylfuran: Derived from abundant carbohydrates



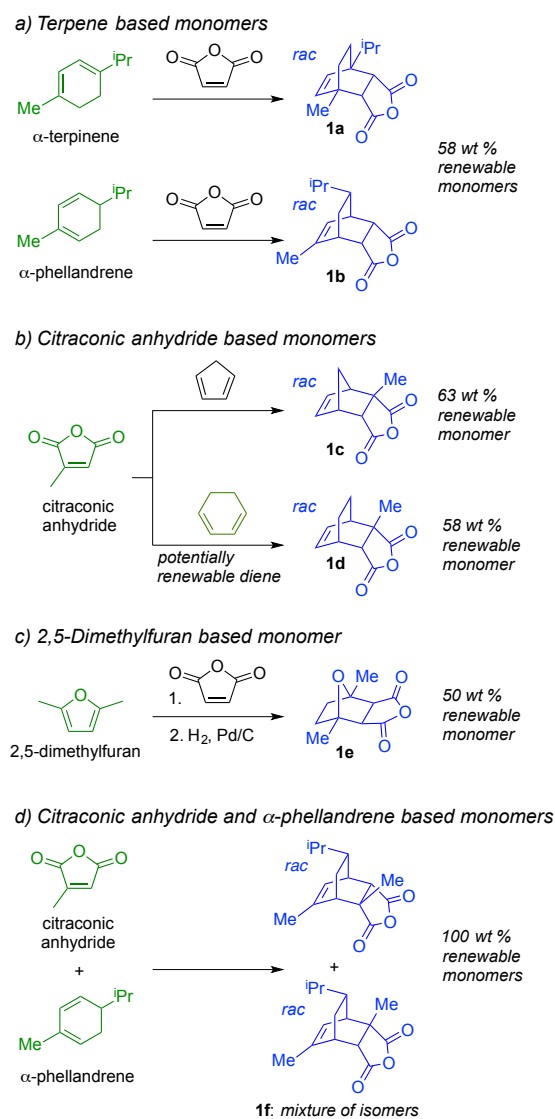
Citraconic Anhydride: Produced from biosourced itaconic acid



On the basis of our previous work,^{16c,16d} and the range of renewable dienes and dienophiles available, we chose to focus on tricyclic anhydrides due to their well-controlled polymerization behavior and typically higher T_g values due to rigidity of the anhydride unit. We synthesized six partially or fully renewable anhydrides based on α -terpinene, α -phellandrene, citraconic anhydride, and 2,5-dimethylfuran. Terpenes such as α -terpinene and α -phellandrene (Scheme 2) are part of a class of naturally occurring molecules synthesized through biosynthetic pathways, that have been extensively investigated as renewable building blocks.²⁰ Dehydration and subsequent hydrogenolysis of carbohydrates leads to 2,5-dimethylfuran (Scheme 2) that has been investigated as a potential renewable liquid fuel.²¹ Citraconic anhydride (Scheme 2) is produced from the isomerization and dehydration of itaconic acid.²² This naturally occurring acid, which is

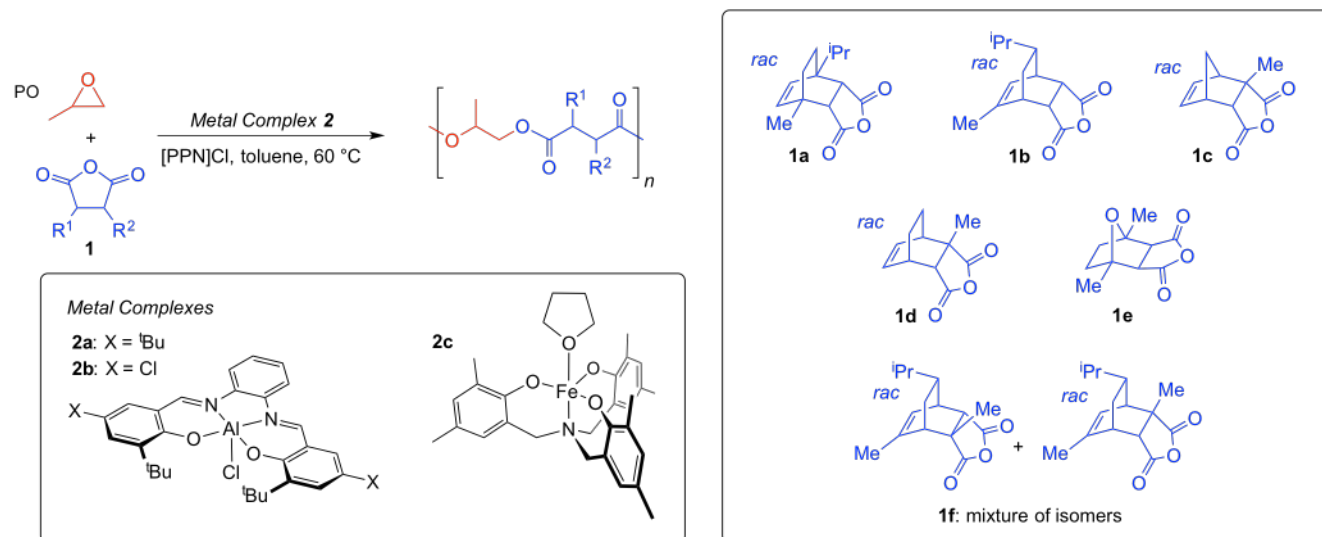
commonly produced industrially by fermentation of carbohydrates,²³ is one of the U.S. Department of Energy's top twelve value added chemicals derived from biomass.²⁴

Scheme 3. Synthesis of partially renewable tricyclic anhydrides from a) terpenes, b) citraconic anhydride, c) 2,5-dimethylfuran, and d) completely renewable tricyclic anhydrides.



We used the renewable precursors in Scheme 2 to synthesize five tricyclic anhydrides (**1a–1e**) through Diels-Alder reactions, creating a series of anhydrides that are 50–63% renewable by mass (Scheme 3a–c). Monomer **1d** has the potential to be completely renewable, as 1,3-

1
2
3 cyclohexadiene has been synthesized through the metathesis of plant oils.²⁵ The Diels-Alder
4
5 adduct of maleic anhydride and 2,5-dimethylfuran undergoes a rapid retro Diels-Alder reaction
6
7
8 in the presence of Lewis acidic catalysts, so it was saturated via catalytic hydrogenation to access
9
10 an anhydride stable enough for polymerization. We also synthesized a completely renewable
11
12 anhydride through the Diels-Alder reaction of citraconic anhydride and α -phellandrene. This
13
14 reaction yielded an inseparable mixture of structural isomers in a 54:46 ratio (**1f**, Scheme 3d).
15
16
17 This mixture of isomers may aid in achieving the desired rigid, completely amorphous polymer
18
19 backbone. Other Diels-Alder reactions between combinations of renewable dienes and
20
21 dieneophiles that would have yielded completely renewable anhydrides (e.g. citraconic
22
23 anhydride and α -terpinene or 2,5-dimethylfuran) were not successful under routine conditions,
24
25
26 likely due to steric bulk hindering the reaction.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 1. Copolymerization of **1a–1f** with propylene oxide (PO).

Entry	Anhyd.	Complex	t_{rxn} (h)	Conv. (%) ^b	M_n (kDa) ^c	\bar{D} ^c	T_g (°C) ^d	% <i>cis</i> ^e
1	1a	2a	5	>99	29.2	1.10	108	>99
2	1a	2c	6	>99	15.3	1.13	103	>99
3	1b	2b	10	>99	30.0	1.12	91	>99
4	1b	2c	6	>99	17.2	1.10	91	>99
5	1c	2a	3.5	>99	32.2	1.07	79	>99
6	1c	2c	6	>99	11.1	1.14	74	>99
7	1d	2a	4	>99	28.1	1.12	86	>99
8	1d	2c	8	>99	10.5	1.11	66	>99
9	1e	2b	18	>99	29.8	1.10	92	>99
10	1e	2c	5.5	>99	10.4	1.28	86	36
11	1f	2a	3.5	>99	18.7	1.10	100	>99
12	1f	2c	7	>99	11.3	1.11	90	>99

^a [PO]:[1]:[2]:[PPN]Cl] = 1500:300:1:0.9 ^b Conversion of cyclic anhydride, determined by ¹H NMR spectroscopy. ^c Determined by GPC in THF, at 30 °C, calibrated with polystyrene standards. ^d Determined by DSC; reported T_g values are from the second heat. ^e Determined by ¹H NMR spectroscopy of the mixture of diols obtained from the reductive degradation of the polymer with LiAlH₄.

We first polymerized all six anhydrides with propylene oxide (PO). Previous work showed that the copolymerization of **1a** with PO yielded a polymer with a T_g up to 109 °C,^{16c} leading us to believe that we could achieve similarly high T_g values with the other five anhydrides. Excess

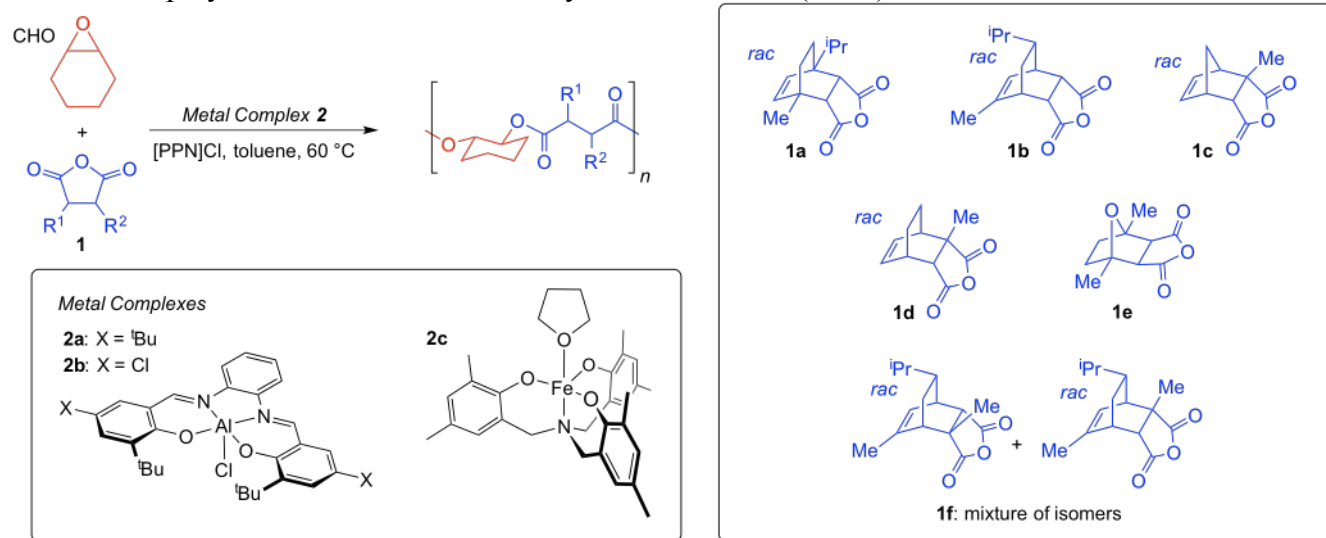
1
2
3 epoxide was used because it is easier to remove from the polymer than solid anhydride and
4
5 allowed the polymerizations to be run neat, increasing the polymerization rate. Since both
6
7 catalytic systems had previously shown high selectivity for polyester^{16c,d} or polycarbonate¹⁸
8
9 formation, we could use excess epoxide without favoring homopolymerization.
10
11

12
13 With PO, the six anhydrides gave perfectly alternating copolymers with T_g values ranging from
14
15 66 to 108 °C (Table 1). The resulting polymers exhibited molecular weights up to 32.2 kDa and
16
17 D values below 1.15, with the exception of poly(PO-*alt*-**1e**) synthesized with **2c** (Table 1, Entry
18
19 10), which had a broader dispersity ($D = 1.28$). Consistent with our previous work,^{16d} we found
20
21 that an electron-withdrawing complex (**2b**) was necessary for the less bulky anhydrides (**1b**, **1e**)
22
23 in order to avoid side-reactions at high conversion. Bulkier anhydrides (**1a**, **1c**, **1d**, **1f**) could be
24
25 copolymerized using **2a** without significant side reactions; these anhydrides required much
26
27 longer reaction times when using complex **2b**. We found that in general **2c** gave lower molecular
28
29 weights than either **2a** or **2b**, and that both systems gave bimodal GPC traces. We propose this
30
31 could be due to the presence of adventitious water which can react with anhydrides to form
32
33 diacids, or chain shuttle with a metal alkoxide ultimately forming a diol, both of which can
34
35 generate new, bifunctional, polymer chains giving rise to a second distribution which is double
36
37 the molecular weight of Cl⁻ initiated chains.²⁶ This increase in the number of chains can depress
38
39 the overall molecular weight. We found that **2c** was intermediate in rate being slower than **2a** for
40
41 monomers **1a**, **1c**, **1d**, and **1f** and faster than **2b** for monomers **1b** and **1e**. All of the polymers
42
43 retained a high *cis*-diester contents (>99%) even at full conversion with the exception of
44
45 poly(PO-*alt*-**1e**) synthesized with **2c**, which had only 36% *cis*-diester linkages at full conversion
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60 (Table 1, Entry 10).

1
2
3 The T_g values ranged from 66 °C for a low molecular weight sample of poly(PO-*alt*-**1d**) (Table
4 1, Entry 8), to 108 °C for the higher molecular weight sample of poly(PO-*alt*-**1a**) (Table 1, Entry
5 1). The highest T_g samples were made with the bulkiest anhydrides (**1a** and **1f**) suggesting that
6 increased bulk along the polymer backbone increased the T_g as expected. Poly(PO-*alt*-**1a**) and
7 poly(PO-*alt*-**1f**) are of particular interest as they have T_g values higher than or comparable to that
8 of widely used polystyrene ($T_g = 100$ °C), respectively. Although there were some differences in
9 T_g between samples synthesized with the Al and Fe complexes, the differences in T_g are
10 attributable to disparities in molecular weight. In general, the Al and Fe complexes gave similar
11 reactivity, although the Fe complex gave lower molecular weight materials overall.
12
13
14
15
16
17
18
19
20
21
22
23

24 One of the advantages of epoxide/anhydride copolymerizations is that polymer properties can
25 be tuned not only through the anhydride, but also through the epoxide. Thus, while the polymers
26 produced with PO had T_g values up to 35 °C higher than that of PLA, we hoped to further
27 increase the T_g by switching to a bulkier, more rigid epoxide. Cyclohexene oxide (CHO) has
28 been shown to give high T_g polycarbonates ($T_g \sim 122$ °C) when alternating copolymerized with
29 CO_2 ,²⁷ which made it a promising choice. A recent report on the copolymerization of a similar
30 tricyclic anhydride and CHO found that the resulting polymer had a T_g up to 129 °C.¹⁰
31 Additionally, while CHO is not currently considered renewable, it could potentially be
32 synthesized from renewable sources through metathesis of plant oils to form 1,4-cyclohexadiene
33 and subsequent epoxidation and hydrogenation.^{11f, 25} We screened all six anhydrides with CHO
34 (Table 2) and observed a significant increase in T_g compared to the corresponding polymers
35 synthesized with PO (Table 1). We found that reducing the amount of CHO from 1500 to 900 eq
36 and replacing the volume with toluene led to higher molecular weights and narrower D values,²⁸
37 with T_g values ranging from 124 to 184 °C. Similar to the PO based polymers, poly(CHO-*alt*-**1a**)
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 and poly(CHO-*alt*-**1f**) had the highest T_g values (Table 2, Entries 1-2 and 11-12; up to 184 °C
4
5 and 165 °C respectively), which to the best of our knowledge are the highest reported T_g values
6
7
8 for aliphatic polyesters synthesized through chain-growth polymerization.
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table 2. Copolymerization of **1a–1f** with cyclohexene oxide (CHO).

Entry	Anhyd.	Complex	t_{rxn} (h)	Conv. (%) ^b	M_n (kDa) ^c	\bar{D} ^c	T_g (°C) ^d	% <i>cis</i> ^e
1 ^f	1a	2a	60	96	8.9	1.27	184	>99
2	1a	2c	168	68	4.1	1.30	162	>99
3	1b	2a	24	>99	12.2	1.40	156	>99
4	1b	2c	20	>99	11.6	1.37	151	>99
5	1c	2a	15	>99	10.9	1.46	149	>99
6	1c	2c	20	>99	8.6	1.23	149	>99
7	1d	2a	10	>99	9.4	1.40	162	>99
8	1d	2c	23	>99	9.9	1.58	158	>99
9	1e	2a	48	>99	7.3	1.46	128	>99
10	1e	2c	20	>99	9.7	1.31	124	>99
11	1f	2a	25	>99	9.5	1.24	165	>99
12	1f	2c	15	>99	6.4	1.36	140	>99

^a [CHO]:[**1**]:[**2**]:[PPN]Cl] = 900:300:1:0.9 ^b Conversion of cyclic anhydride, determined by ¹H NMR spectroscopy. ^c Determined by GPC in THF, at 30 °C, calibrated with polystyrene standards. ^d Determined by DSC; reported T_g values are from the second heat. ^e Determined by ¹H NMR spectroscopy of the mixture of diols obtained from the reductive degradation of the polymer with LiAlH₄. ^f Polymerization run at 70 °C.

The polymerization rates were significantly lower with CHO, likely due to the increased bulk of the epoxide, and the Al and Fe complexes in general had much more comparable rates with CHO than with PO. Complex **2b** was markedly slower than **2a** with CHO, and since no

1
2
3 epimerization was observed with **2a** (Table 2), likely due to increased steric hindrance, **2a** was
4
5 used for all monomer sets. With **1a**, we were unable to reach high conversion using complex **2a**
6
7 at 60 °C, even at extended reaction times. We subsequently increased the reaction temperature to
8
9 70 °C and were able to achieve 96% conversion (Table 2, Entry 1).
10
11

12
13 A limitation of the CHO based polymers is their relatively low molecular weights; poly(CHO-
14
15 *alt-1b*) synthesized with complex **2a** had the highest molecular weight at a modest 12.2 kDa
16
17 (Table 2, Entry 3). Analysis by MALDI-TOF-MS for all samples in Table 2 revealed the
18
19 complete absence of cyclic structures (Figure S26 and S27). In fact, all samples had the expected
20
21 α,ω -Cl,OH end groups and did not contain any end groups consistent with transesterification
22
23 such as cyclic structures or α,ω -Cl,Cl end groups.²⁹ To our surprise, there was an additional set
24
25 of signals in the spectra corresponding to polymers without the expected chloride end group. We
26
27 propose that this could be due to a Meerwein–Ponndorf–Verley–Oppenauer (MPVO) type
28
29 reaction occurring and generating CHO based alcohols that can initiate new polymer chains, as
30
31 previously reported by Duchateau.^{13i,30} The resulting increase in the number of initiators would
32
33 account for the lowered molecular weights compared to the PO based polymers. Additionally, if
34
35 alcohol was being slowly generated throughout the polymerization, new chains would be
36
37 generated over the course of the polymerization leading to generally higher D values for the
38
39 CHO polymers (Table 2, $D = 1.20$ – 1.58).³¹
40
41
42
43
44
45

46
47 In conclusion, we have synthesized six tricyclic anhydrides that were either partially (50–63%
48
49 by weight) or fully renewably sourced and successfully used them in alternating
50
51 copolymerizations with propylene oxide, an inexpensive, readily available monomer, and with
52
53 cyclohexene oxide, which has the potential to be renewably sourced. By varying both the
54
55 epoxide and the anhydride, we were able to tune the T_g of the resulting polymers over a nearly
56
57
58
59
60

1
2
3 120 °C range from 66 °C to an exceptionally high 184 °C. Polymers synthesized with PO had
4
5 higher polymerization rates, narrower D values, and higher molecular weights, albeit with
6
7 generally lower T_g values (66–108 °C). CHO containing polymers had significantly higher T_g
8
9 values, (124–184 °C) although they had lower molecular weights, broader D values, and
10
11 substantially decreased polymerization rates. To the best of our knowledge, these are the highest
12
13 T_g values reported for entirely aliphatic polyesters. The high T_g values of these materials give
14
15 them potential for use in a variety of higher temperature applications. In addition to exploring
16
17 other potential renewable monomers, we are currently investigating further catalyst development
18
19 to allow access to higher molecular weight CHO based polymers, as well as examining the
20
21 physical and mechanical properties of these materials.
22
23
24
25
26
27
28
29

30 ASSOCIATED CONTENT

31 32 33 **Supporting Information**

34
35
36 Polymerization procedures, synthetic procedures, MALDI-TOF-MS data, GPC traces, DSC
37
38 traces, TGA analysis of polymers, supplementary experiments, and NMR characterization data.

39
40 The Supporting Information is available free of charge on the ACS Publications website.
41
42
43

44 AUTHOR INFORMATION

45 46 47 **Corresponding Author**

48
49 * coates@cornell.edu

50
51
52
53 * akleij@iciq.es
54
55
56
57
58
59
60

Present Addresses

† Institute for Complex Molecular Systems and Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Funding for this project was provided by the Center for Sustainable Polymers, an NSF Center for Chemical Innovation (CHE-1413862). N.J.V.Z. acknowledges the NSF for financial support through the IGERT program (DGE-0903653). L.P.C. and A.W.K. acknowledge the Spanish Ministerio de Economía y Competitividad (MINECO) for financial support through project CTQ-2014-60419-R and for FPI and EEBB fellowships. Severo Ochoa Excellence Accreditation 2014-2018 is acknowledged for financial support through project SEV-2013-0319. Dr. Noemí Cabello is acknowledged for the MALDI-TOF analyses. This work made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (DMR-1120296). We thank Kyle O'Connor for helpful discussions.

REFERENCES

(1) (a) Gandini, A. The irruption of polymers from renewable resources on the scene of macromolecular science and technology. *Green Chem.* **2011**, *13*, 1061–1083. (b) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T.

1
2
3
4 The Path Forward for Biofuels and Biomaterials. *Science* **2006**, *311*, 484–489. (c) Mecking, S.
5
6 Nature or Petrochemistry?—Biologically Degradable Materials. *Angew. Chem., Int. Ed.* **2004**,
7
8 *43*, 1078–1085. (d) Gross, R. A.; Kalra, B. Biodegradable Polymers for the Environment.
9
10 *Science* **2002**, *297*, 803–807.
11
12

13
14 (2) (a) Hillmyer, M. A.; Tolman, W. B. Aliphatic Polyester Block Polymers: Renewable,
15
16 Degradable, and Sustainable. *Acc. Chem. Res.* **2014**, *47*, 2390–2396. (b) Vert, M. Aliphatic
17
18 Polyesters: Great Degradable Polymers That Cannot Do Everything. *Biomacromolecules* **2005**,
19
20 *6*, 538–546. (c) Amass, W.; Amass, A.; Tighe, B. A review of biodegradable polymers: uses,
21
22 current developments in the synthesis and characterization of biodegradable polyesters, blends of
23
24 biodegradable polymers and recent advances in biodegradation studies. *Polym. Int.* **1998**, *47*, 89–
25
26 144.
27
28
29
30

31
32 (3) (a) Olson, D. A.; Gratton, S. E. A.; DeSimone, J. M.; Sheares, V. V. Amorphous Linear
33
34 Aliphatic Polyesters for the Facile Preparation of Tunable Rapidly Degrading Elastomeric
35
36 Devices and Delivery Vectors. *J. Am. Chem. Soc.* **2006**, *128*, 13625–13633. (b) Müller, R.-J.;
37
38 Kleeberg, I.; Deckwer, W.-D. Biodegradation of polyesters containing aromatic constituents. *J.*
39
40 *Biotechnol.* **2001**, *86*, 87–95. (c) Brown, A. H.; Sheares, V. V. Amorphous Unsaturated Aliphatic
41
42 Polyesters Derived from Dicarboxylic Monomers Synthesized by Diels–Alder Chemistry.
43
44 *Macromolecules* **2007**, *40*, 4848–4853.
45
46
47
48

49
50 (4) Lecomte, P.; Jérôme, C. In *Synthetic Biodegradable Polymers*; Rieger, B., Künkel, A.,
51
52 Coates, W. G., Reichardt, R., Dinjus, E., Zevaco, A. T., Eds.; Springer Berlin Heidelberg: Berlin,
53
54 Heidelberg, 2012, p 173-217.
55
56
57
58
59
60

1
2
3
4 (5) (a) Engels, H.-W.; Pirkl, H.-G.; Albers, R.; Albach, R. W.; Krause, J.; Hoffmann, A.;
5 Casselmann, H.; Dormish, J. Polyurethanes: Versatile Materials and Sustainable Problem Solvers
6 for Today's Challenges. *Angew. Chem., Int. Ed.* **2013**, *52*, 9422–9441. (b) Gupta, A. P.; Kumar,
7 V. New emerging trends in synthetic biodegradable polymers – Polylactide: A critique. *Eur.*
8 *Polym. J.* **2007**, *43*, 4053–4074. (c) Datta, R.; Henry, M. Lactic acid: recent advances in
9 products, processes and technologies — a review. *J. Chem. Technol. Biotechnol.* **2006**, *81*,
10 1119–1129. (d) Auras, R.; Harte, B.; Selke, S. An Overview of Polylactides as Packaging
11 Materials. *Macromol. Biosci.* **2004**, *4*, 835–864. (e) Vink, E. T. H.; Rábago, K. R.; Glassner, D.
12 A.; Gruber, P. R. Applications of life cycle assessment to NatureWorks™ polylactide (PLA)
13 production. *Polym. Degrad. Stab.* **2003**, *80*, 403–419. (f) Ikada, Y.; Tsuji, H. Biodegradable
14 polyesters for medical and ecological applications. *Macromol. Rapid Commun.* **2000**, *21*, 117–
15 132.

16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34 (6) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-opening
35 copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem.*
36 *Commun.* **2015**, *51*, 6459–6479.

37
38
39
40
41
42 (7) (a) Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. Polymers
43 from renewable 1,4:3,6-dianhydrohexitols (isosorbide, isomannide and isoidide): A review.
44 *Prog. Polym. Sci.* **2010**, *35*, 578–622. (b) Storbeck, R.; Ballauff, M. Synthesis and properties of
45 polyesters based on 2,5-furandicarboxylic acid and 1,4:3,6-dianhydrohexitols. *Polymer* **1993**, *34*,
46 5003–5006.

47
48
49
50
51
52
53
54 (8) Fiore, G. L.; Jing, F.; Young, J. V. G.; Cramer, C. J.; Hillmyer, M. A. High T_g aliphatic
55 polyesters by the polymerization of spirolactide derivatives. *Polym. Chem.* **2010**, *1*, 870–877.
56
57
58
59
60

1
2
3
4 (9) Lavilla, C.; Alla, A.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. High T_g Bio-Based
5 Aliphatic Polyesters from Bicyclic d-Mannitol. *Biomacromolecules* **2013**, *14*, 781–793.
6
7

8
9
10 (10) Han, B.; Zhang, L.; Liu, B.; Dong, X.; Kim, I.; Duan, Z.; Theato, P. Controllable
11 Synthesis of Stereoregular Polyesters by Organocatalytic Alternating Copolymerizations of
12 Cyclohexene Oxide and Norbornene Anhydrides. *Macromolecules* **2015**, *48*, 3431–3437.
13
14

15
16
17 (11) (a) Zhu, L.; Liu, D.; Wu, L.; Feng, W.; Zhang, X.; Wu, J.; Fan, D.; Lü, X.; Lu, R.; Shi, Q.
18 A trinuclear $[Zn_3(L)_2(OAc)_2]$ complex based on the asymmetrical bis-Schiff-base ligand H_2L for
19 ring-opening copolymerization of CHO and MA. *Inorg. Chem. Commun.* **2013**, *37*, 182–185. (b)
20 Liu, D.-F.; Wu, L.-Y.; Feng, W.-X.; Zhang, X.-M.; Wu, J.; Zhu, L.-Q.; Fan, D.-D.; Lü, X.-Q.;
21 Shi, Q. Ring-opening copolymerization of CHO and MA catalyzed by mononuclear
22 $[Zn(L_2)(H_2O)]$ or trinuclear $[Zn_3(L_2)_2(OAc)_2]$ complex based on the asymmetrical bis-Schiff-base
23 ligand precursor. *J. Mol. Catal. A: Chem.* **2014**, *382*, 136–145. (c) Liu, Y.; Xiao, M.; Wang, S.;
24 Xia, L.; Hang, D.; Cui, G.; Meng, Y. Mechanism studies of terpolymerization of phthalic
25 anhydride, propylene epoxide, and carbon dioxide catalyzed by ZnGA. *RSC Advances* **2014**, *4*,
26 9503–9508. (d) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. Di-magnesium and zinc
27 catalysts for the copolymerization of phthalic anhydride and cyclohexene oxide. *Polym. Chem.*
28 **2014**, *5*, 6068–6075. (e) Wu, L.-y.; Fan, D.-d.; Lü, X.-q.; Lu, R. Ring-opening copolymerization
29 of cyclohexene oxide and maleic anhydride catalyzed by mononuclear $[Zn(L)(H_2O)]$ or binuclear
30 $[Zn_2(L)(OAc)_2(H_2O)]$ complex based on the Salen-type Schiff-base ligand. *Chin. J. Polym. Sci.*
31 **2014**, *32*, 768–777. (f) Winkler, M.; Romain, C.; Meier, M. A. R.; Williams, C. K. Renewable
32 polycarbonates and polyesters from 1,4-cyclohexadiene. *Green Chem.* **2015**, *17*, 300–306. (g)
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Zhu, Y.; Romain, C.; Williams, C. K. Selective Polymerization Catalysis: Controlling the Metal

1
2
3
4 Chain End Group to Prepare Block Copolyesters. *J. Am. Chem. Soc.* **2015**, *137*, 12179–12182.

5
6 (h) Thevenon, A.; Garden, J. A.; White, A. J. P.; Williams, C. K. Dinuclear Zinc Salen Catalysts
7
8 for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides. *Inorg.*
9
10 *Chem.* **2015**, *54*, 11906–11915. (i) Garden, J. A.; Saini, P. K.; Williams, C. K. Greater than the
11
12 Sum of Its Parts: A Heterodinuclear Polymerization Catalyst. *J. Am. Chem. Soc.* **2015**, *137*,
13
14 15078–15081.
15
16
17

18
19 (12) Takasu, A.; Ito, M.; Inai, Y.; Hirabayashi, T.; Nishimura, Y. Synthesis of Biodegradable
20
21 Polyesters by Ring-Opening Copolymerization of Cyclic Anhydrides Containing a Double Bond
22
23 with 1,2-Epoxybutane and One-Pot Preparation of the Itaconic Acid-Based Polymeric Network.
24
25 *Polym. J.* **1999**, *31*, 961–969.
26
27

28
29 (13) (a) Huijser, S.; HosseiniNejad, E.; Sablong, R.; de Jong, C.; Koning, C. E.; Duchateau, R.
30
31 Ring-Opening Co- and Terpolymerization of an Alicyclic Oxirane with Carboxylic Acid
32
33 Anhydrides and CO₂ in the Presence of Chromium Porphyrinato and Salen Catalysts.
34
35 *Macromolecules* **2011**, *44*, 1132–1139. (b) Robert, C.; de Montigny, F.; Thomas, C. M. Tandem
36
37 synthesis of alternating polyesters from renewable resources. *Nat. Commun.* **2011**, *2*, 586. (c)
38
39 Darensbourg, D. J.; Poland, R. R.; Escobedo, C. Kinetic Studies of the Alternating
40
41 Copolymerization of Cyclic Acid Anhydrides and Epoxides, and the Terpolymerization of Cyclic
42
43 Acid Anhydrides, Epoxides, and CO₂ Catalyzed by (salen)Cr^{III}Cl. *Macromolecules* **2012**, *45*,
44
45 2242–2248. (d) Hosseini Nejad, E.; Paoniasari, A.; Koning, C. E.; Duchateau, R. Semi-aromatic
46
47 polyesters by alternating ring-opening copolymerisation of styrene oxide and anhydrides. *Polym.*
48
49 *Chem.* **2012**, *3*, 1308–1313. (e) Hosseini Nejad, E.; van Melis, C. G. W.; Vermeer, T. J.; Koning,
50
51 C. E.; Duchateau, R. Alternating Ring-Opening Polymerization of Cyclohexene Oxide and
52
53
54
55
56
57
58
59
60

1
2
3
4 Anhydrides: Effect of Catalyst, Cocatalyst, and Anhydride Structure. *Macromolecules* **2012**, *45*,
5 1770–1776. (f) Bernard, A.; Chatterjee, C.; Chisholm, M. H. The influence of the metal (Al, Cr
6 and Co) and the substituents of the porphyrin in controlling the reactions involved in the
7 copolymerization of propylene oxide and cyclic anhydrides by porphyrin metal(III) complexes.
8
9
10
11
12
13
14 *Polymer* **2013**, *54*, 2639–2646. (g) Harrold, N. D.; Li, Y.; Chisholm, M. H. Studies of Ring-
15
16 Opening Reactions of Styrene Oxide by Chromium Tetraphenylporphyrin Initiators. Mechanistic
17 and Stereochemical Considerations. *Macromolecules* **2013**, *46*, 692–698. (h) Liu, J.; Bao, Y.-Y.;
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

(14) Longo, J. M.; DiCiccio, A. M.; Coates, G. W. Poly(propylene succinate): A New Polymer
Stereocomplex. *J. Am. Chem. Soc.* **2014**, *136*, 15897–15900.

(15) (a) Robert, C.; Ohkawara, T.; Nozaki, K. Manganese-Corrole Complexes as Versatile
Catalysts for the Ring-Opening Homo- and Co-Polymerization of Epoxide. *Chem. - Eur. J.* **2014**,
20, 4789–4795. (b) Liu, D.-F.; Zhu, L.-Q.; Wu, J.; Wu, L.-Y.; Lu, X.-Q. Ring-opening

1
2
3
4 copolymerization of epoxides and anhydrides using manganese(iii) asymmetrical Schiff base
5 complexes as catalysts. *RSC Advances* **2015**, *5*, 3854–3859. (c) Liu, D.; Zhang, Z.; Zhang, X.;
6
7 Lü, X. Alternating Ring-Opening Copolymerization of Cyclohexene Oxide and Maleic
8 Anhydride with Diallyl-Modified Manganese(iii)–Salen Catalysts. *Aust. J. Chem.* **2016**, *69*, 47–
9
10
11
12
13
14 55.

15
16
17 (16) (a) Aida, T.; Inoue, S. Catalytic reaction on both sides of a metalloporphyrin plane.
18 Alternating copolymerization of phthalic anhydride and epoxypropane with an aluminum
19 porphyrin-quaternary salt system. *J. Am. Chem. Soc.* **1985**, *107*, 1358–1364. (b) Aida, T.;
20 Sanuki, K.; Inoue, S. Well-controlled polymerization by metalloporphyrin. Synthesis of
21 copolymer with alternating sequence and regulated molecular weight from cyclic acid anhydride
22 and epoxide catalyzed by the system of aluminum porphyrin coupled with quaternary organic
23 salt. *Macromolecules* **1985**, *18*, 1049–1055. (c) Van Zee, N. J.; Coates, G. W. Alternating
24 Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A
25 Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures. *Angew.*
26 *Chem., Int. Ed.* **2015**, *54*, 2665–2668. (d) Van Zee, N. J.; Sanford, M. J.; Coates, G. W.
27 Electronic Effects of Aluminum Complexes in the Copolymerization of Propylene Oxide with
28 Tricyclic Anhydrides: Access to Well-Defined, Functionalizable Aliphatic Polyesters. *J. Am.*
29 *Chem. Soc.* **2016**, *138*, 2755–2761.
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

48
49 (17) Whiteoak, C. J.; Gjoka, B.; Martin, E.; Belmonte, M. M.; Escudero-Adán, E. C.; Zonta,
50 C.; Licini, G.; Kleij, A. W. Reactivity Control in Iron(III) Amino Triphenolate Complexes:
51 Comparison of Monomeric and Dimeric Complexes. *Inorg. Chem.* **2012**, *51*, 10639–10649.
52
53
54
55
56
57
58
59
60

1
2
3
4 (18) Taherimehr, M.; Al-Amsyar, S. M.; Whiteoak, C. J.; Kleij, A. W.; Pescarmona, P. P. High
5 activity and switchable selectivity in the synthesis of cyclic and polymeric cyclohexene
6 carbonates with iron amino triphenolate catalysts. *Green Chem.* **2013**, *15*, 3083–3090.
7
8

9
10
11
12 (19) Mundil, R.; Hošťálek, Z.; Šeděnková, I.; Merna, J. Alternating ring-opening
13 copolymerization of cyclohexene oxide with phthalic anhydride catalyzed by iron(III) salen
14 complexes. *Macromol. Res.* **2015**, *23*, 161–166.
15
16
17

18
19
20 (20) (a) Swift, K. A. D. Catalytic Transformations of the Major Terpene Feedstocks. *Top.*
21 *Catal.* **2004**, *27*, 143–155. (b) Behr, A.; Johnen, L. Myrcene as a Natural Base Chemical in
22 Sustainable Chemistry: A Critical Review. *ChemSusChem* **2009**, *2*, 1072–1095. (c) Wilbon, P.
23 A.; Chu, F.; Tang, C. Progress in Renewable Polymers from Natural Terpenes, Terpenoids, and
24 Rosin. *Macromol. Rapid Commun.* **2013**, *34*, 8–37. (d) Dakshinamoorthy, D.; Weinstock, A. K.;
25 Damodaran, K.; Iwig, D. F.; Mathers, R. T. Diglycerol-Based Polyesters: Melt Polymerization
26 with Hydrophobic Anhydrides. *ChemSusChem* **2014**, *7*, 2923–2929. (e) Zhao, J. P.; Schlaad, H.
27 Synthesis of Terpene-Based Polymers. *Adv. Poly. Sci.* **2013**, *253*, 151–190.
28
29
30
31
32
33
34
35
36
37
38
39

40 (21) (a) Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of
41 dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982–985.
42
43 (b) Rasmussen, H.; Sørensen, H. R.; Meyer, A. S. Formation of degradation compounds from
44 lignocellulosic biomass in the biorefinery: sugar reaction mechanisms. *Carbohydr. Res.* **2014**,
45 *385*, 45–57. (c) Chen, M.-Y.; Chen, C.-B.; Zada, B.; Fu, Y. Perovskite type oxide-supported Ni
46 catalysts for the production of 2,5-dimethylfuran from biomass-derived 5-
47 hydroxymethylfurfural. *Green Chem.* **2016**, *18*, 3858–3866.
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4 (22) *The Merck Index*; 14th ed.; Merck & Co., Inc.: Whitehouse Station, NJ, 2006.

5
6
7 (23) Hajian, H.; Yusoff, W. M. W. Itaconic Acid Production by Microorganisms: A Review.
8
9
10 *Curr. Res. J. Biol. Sci.* **2015**, *7*, 37–42.

11
12
13 (24) *Top Value Added Chemicals from Biomass*, U.S. Department of Energy, 2004.
14
15 <http://www.nrel.gov/docs/fy04osti/35523.pdf> (accessed July 3, 2016).

16
17
18 (25) Mathers, R. T.; Shreve, M. J.; Meyler, E.; Damodaran, K.; Iwig, D. F.; Kelley, D. J.
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Synthesis and Polymerization of Renewable 1,3-Cyclohexadiene Using Metathesis,
Isomerization, and Cascade Reactions with Late-metal Catalysts. *Macromol. Rapid Commun.*
2011, *32*, 1338–1342.

(26) Further discussion on the effects of adventitious water and the resulting diacid, a proposed
initiation mechanism (Scheme S1) and representative GPC traces (Figure S25) are in the SI.

(27) (a) Coates, G. W.; Moore, D. R. Discrete Metal-based Catalysts for the Copolymerization
of CO₂ and Epoxides: Discovery, Reactivity, Optimization, and Mechanism. *Angew. Chem. Int.*
Ed. **2004**, *43*, 6618–6639. (b) Kember, M. R.; Buchard, A.; Williams, C. K. Catalysts for
CO₂/epoxide copolymerisation. *Chem. Commun.* **2011**, *47*, 141–163.

(28) For a comparison of polymerizations with and without toluene see Table S1.

(29) MALDI-TOF-MS analysis is shown in the Supporting Information (Figures S26–28).

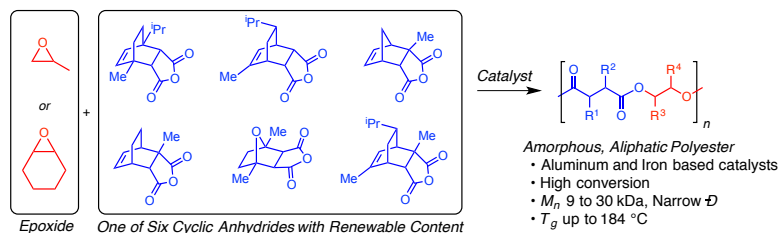
(30) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. Unexpected Side
Reactions and Chain Transfer for Zinc-Catalyzed Copolymerization of Cyclohexene Oxide and
Carbon Dioxide. *Macromolecules* **2005**, *38*, 7306–731.

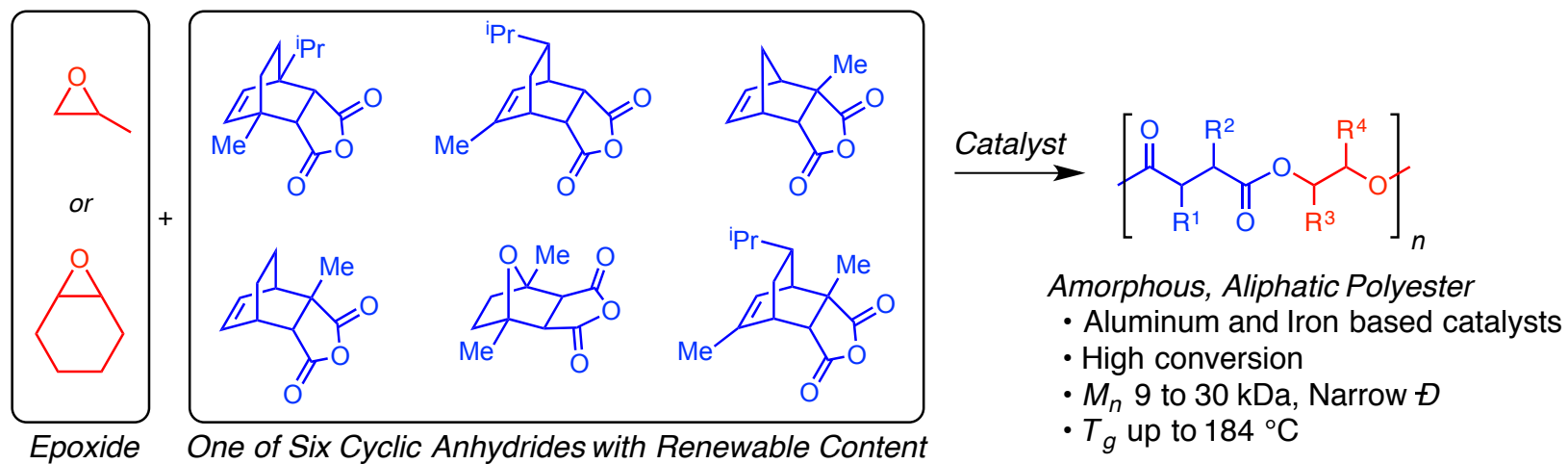
1
2
3
4 (31) Another possible cause of this cyclohexenol end group, decreased M_n values, and increased
5
6 D values is elimination of Cl⁻ from α,ω -Cl,OH terminated polymers. However, as further
7
8 discussed in the SI, while we have not been able to definitively rule out the possibility of
9
10 elimination, we believe that the MPVO reaction is more likely.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

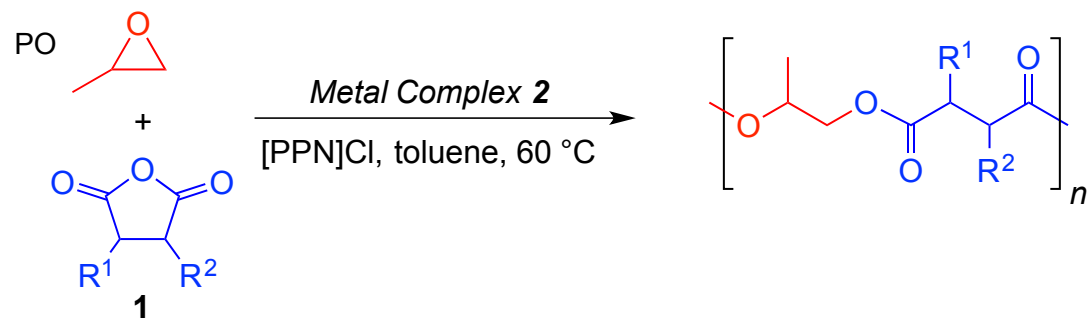
for Table of Contents use only

Alternating Copolymerization of Propylene Oxide and Cyclohexene Oxide with Tricyclic Anhydrides: Access to Partially Renewable Aliphatic Polyesters with High Glass Transition Temperatures

Maria J. Sanford,[‡] Leticia Peña Carrodegua,[§] Nathan J. Van Zee,^{†,‡} Arjan W. Kleij,^{*,§} and Geoffrey W. Coates^{*,‡}



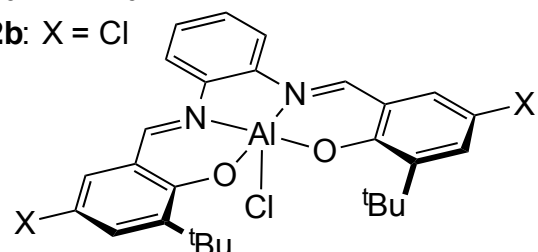




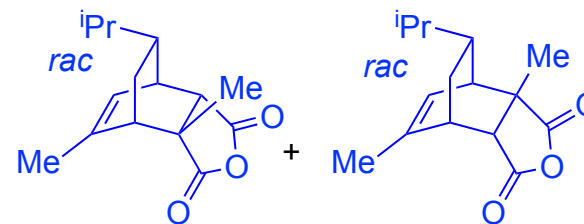
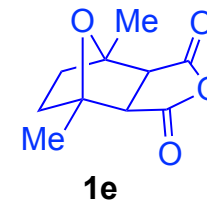
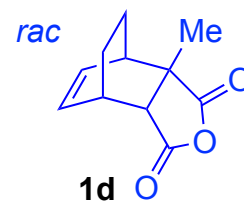
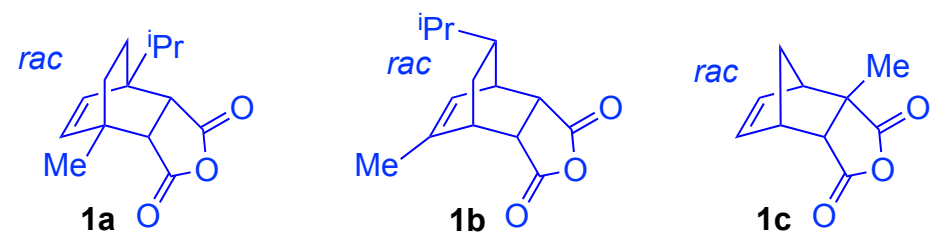
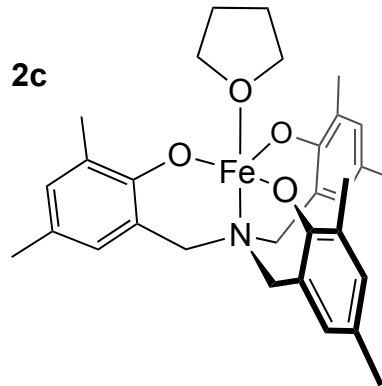
Metal Complexes

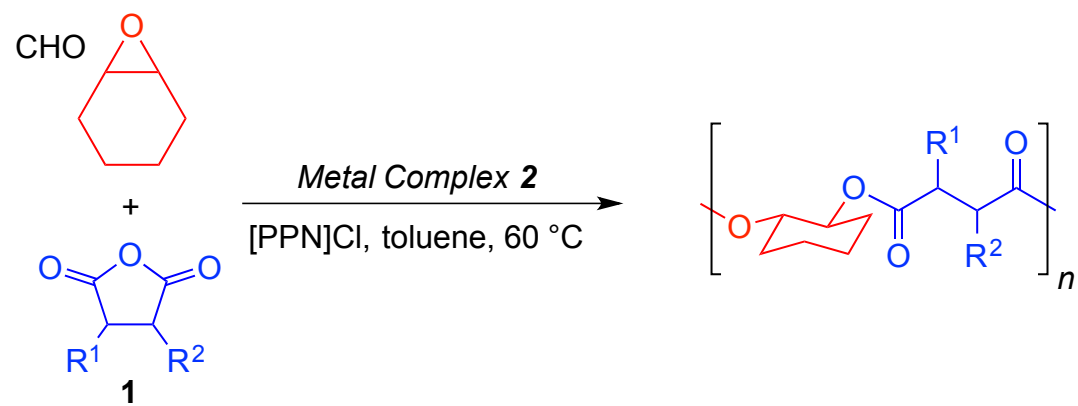
2a: X = ^tBu

2b: X = Cl



2c



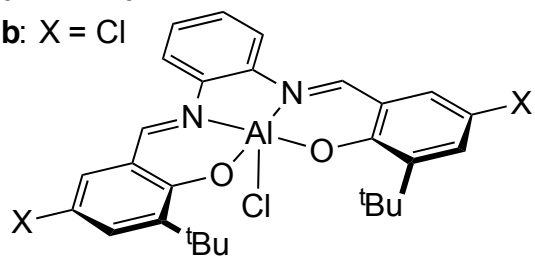


22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

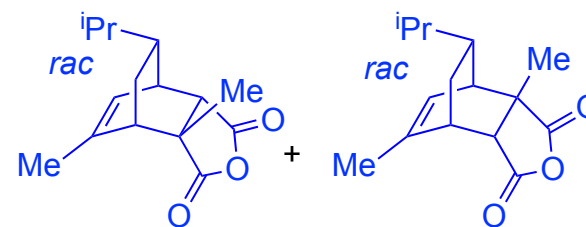
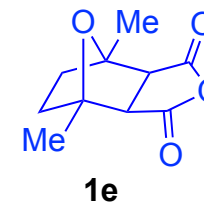
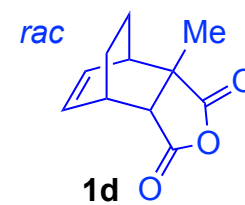
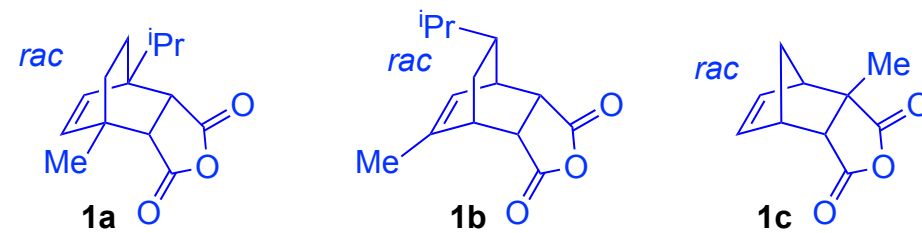
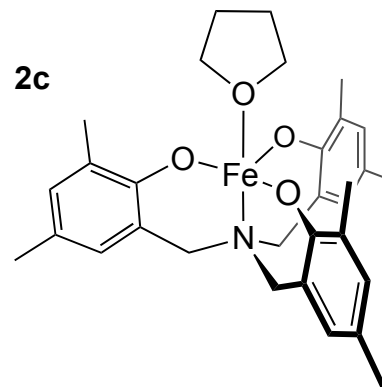
Metal Complexes

2a: X = ^tBu

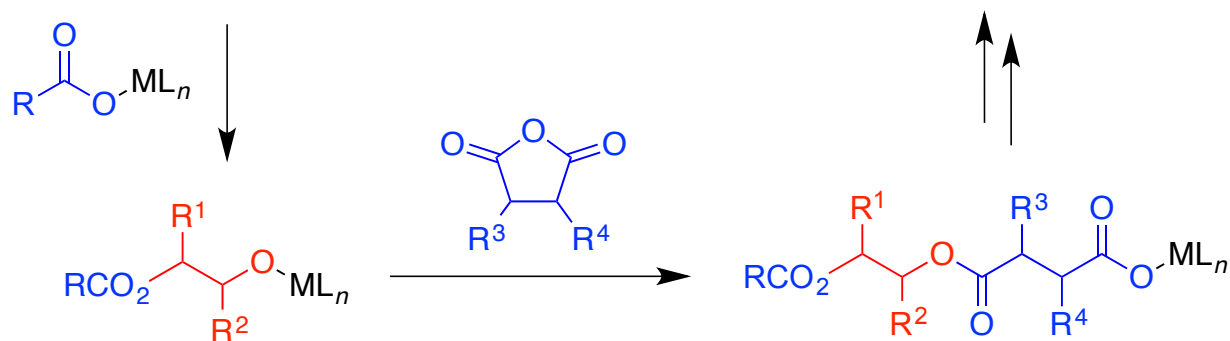
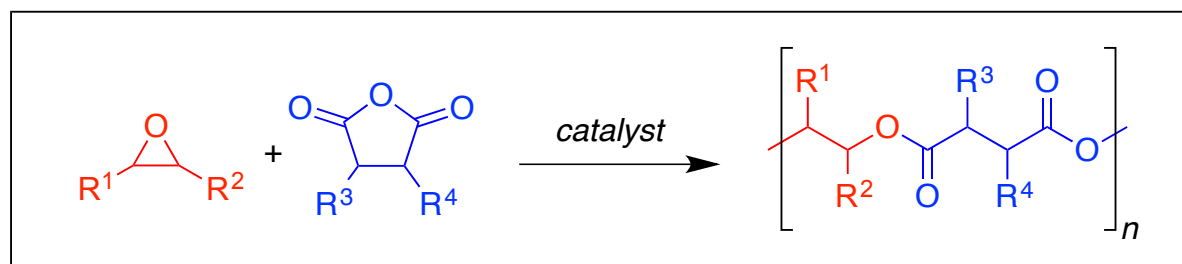
2b: X = Cl



2c

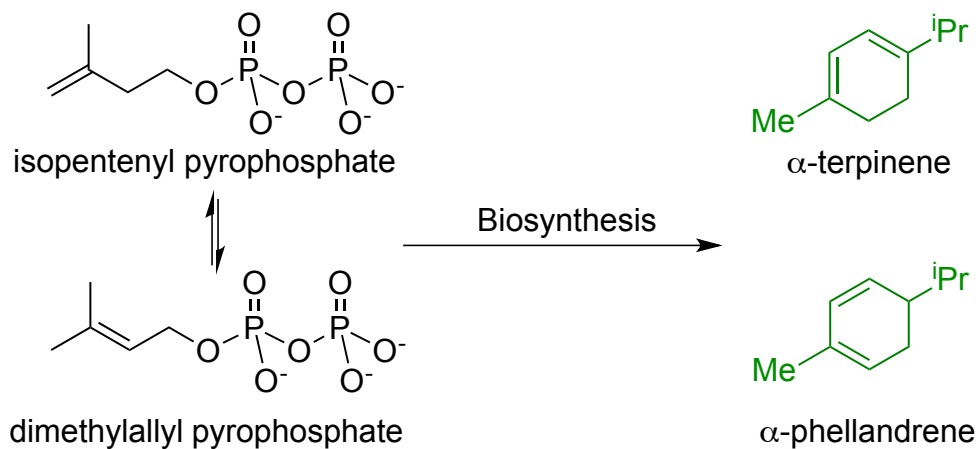


1f: mixture of isomers

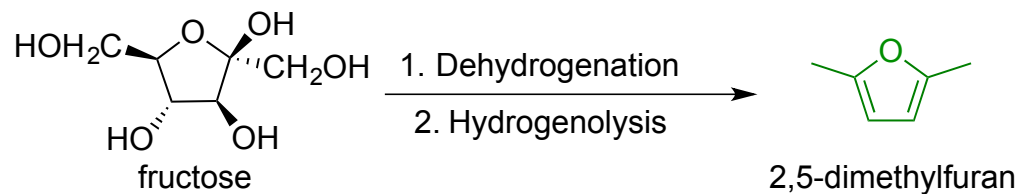


1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

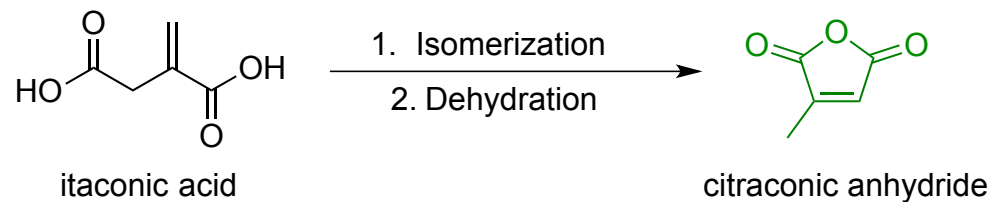
Terpenes: Naturally occurring feedstocks



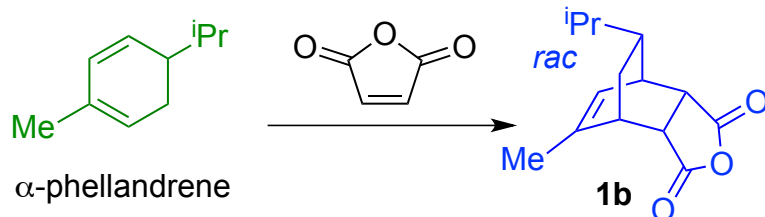
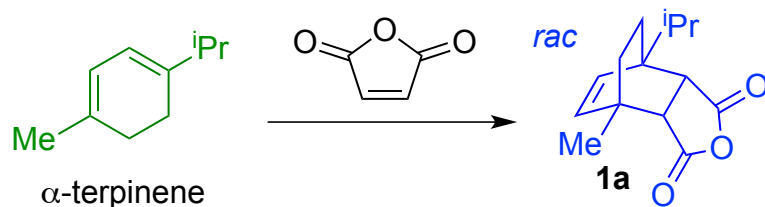
2,5-Dimethylfuran: Derived from abundant carbohydrates



Citraconic Anhydride: Produced from biosourced itaconic acid

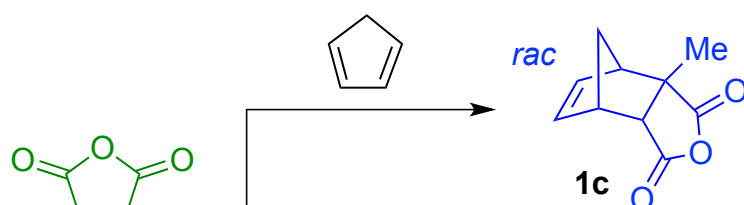


a) Terpene based monomers

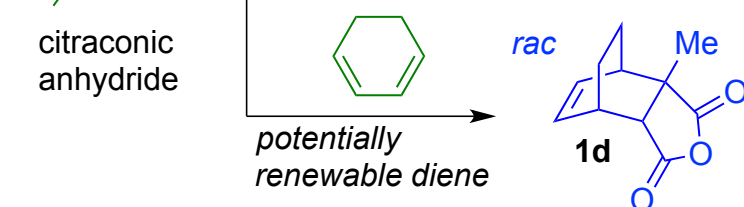


58 wt %
renewable
monomers

b) Citraconic anhydride based monomers

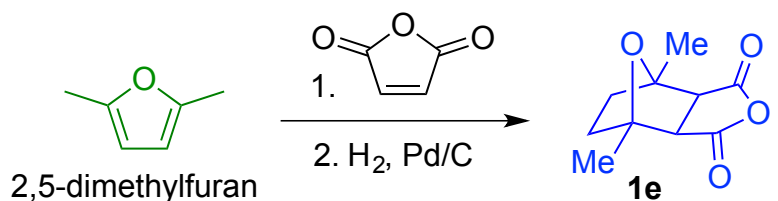


63 wt %
renewable
monomer

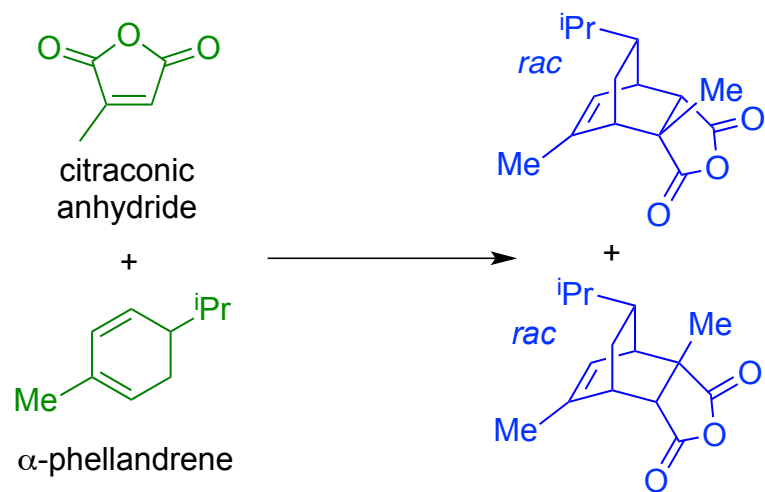


58 wt %
renewable
monomer

c) 2,5-Dimethylfuran based monomer



50 wt %
renewable
monomer

d) Citraconic anhydride and α -phellandrene based monomers

100 wt %
renewable
monomers