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Renewable polycarbonates and polyesters from 1,4-cyclohexadiene†

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Epoxides derived from 1,4-cyclohexadiene (CHD), the latter produced from renewable resources *via* self-metathesis of plant oil derivatives, are applied as key substrates in ring-opening copolymerizations to produce aliphatic polycarbonates and polyesters. Renewable, unsaturated polycarbonates are prepared by the ring-opening copolymerization of epoxide/CO_2; these are catalysed by di-zinc/magnesium complexes previously reported by Williams *et al.* or by using chromium(III) or cobalt(III) salen complexes. Renewable, unsaturated polyesters, with glass transition temperatures up to 128 °C, were obtained by the ring-opening copolymerization of epoxide/phthalic anhydride. The relative rates of these copolymerizations were monitored using *in situ* attenuated total reflectance infra-red (ATR-IR) spectroscopy. The polymers were fully characterized using spectroscopy (nuclear magnetic resonance, infra-red), mass spectrometry (matrix assisted laser desorption ionization), and by thermal methods (differential scanning calorimetry and thermogravimetric analysis).

Introduction

Polycarbonates (PC) are important commodity materials, widely applied in electronics, construction, and as rigid plastics. The most common PC is produced from bisphenol A, which benefits from a high glass transition temperature (149 °C) and good mechanical properties.[1] There are, however, concerns associated with the toxicity of reagents, including the possible endocrine disruptor pathways attributed to BPA. Moreover, such classic PCs are produced *via* polycondensation using phosgene as a co-monomer. This has motivated the quest for alternative materials.

Aliphatic polycarbonates, produced by the metal catalysed alternating ring-opening copolymerization (ROCOP) of CO_2/epoxides (Fig. 1), are attracting considerable attention as semi-renewable polymers.[2] The use of carbon dioxide as a monomer (or generally reagent) is attractive, because it is inexpensive, non-toxic, abundant, renewable and a common waste product of many industrial processes. Although the properties of these materials do not yet match those of PC from bisphenol A, recent research highlights their potential with polymers being produced by this method which show T_g up to 140 °C.[3] Another promising application for such polycarbonates is as low molecular weight polyols (hydroxyl terminated polymers), mainly to be used for the production of polyurethanes. Indeed, poly(ethercarbonate) polyols, produced by ROCOP, have been successfully applied to prepare polyurethane

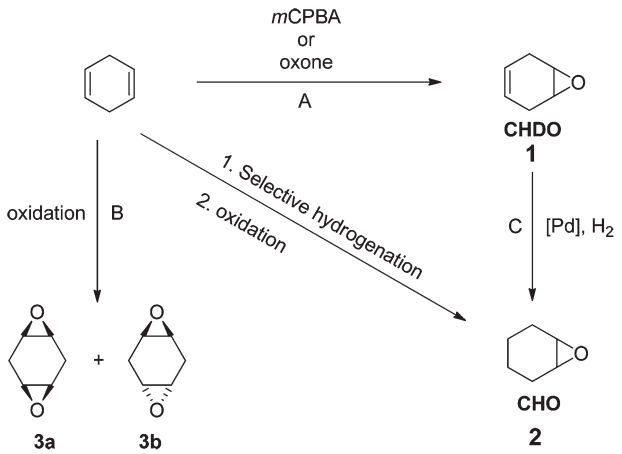

Fig. 1 Synthesis of 1,4-cyclohexadiene oxide (CHDO), cyclohexene oxide (CHO), and two bis-epoxides (*syn*-1,4-cyclohexadiene diepoxide (**3a**), *anti*-1,4-cyclohexadiene diepoxide (**3b**)) from 1,4-cyclohexadiene (CHD). (A) Oxone, DCM/acetone/H_2O/$NaHCO_3$, 298 K, 6 h or *m*CPBA/DCM/H_2O/$NaHCO_3$, 298 K, 6 h, (B) same as for A except the slight excess of mCPBA or Oxone used per double bond, (C) Pd/C(en), 1 wt%, H_2, 298 K, 24 h.

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foams;[4] an in depth life cycle analysis, published this year, found that these materials benefited from reductions in energy use and greenhouse gas emissions of 10–20% compared to conventional polyols.[5]

Considering the sources for the ROCOP monomers, several authors have commented on the ability to use purified carbon dioxide, which might be obtained by carbon capture and sequestration, to prepare the polyols.[4–6] Others have reported catalysts that tolerate high levels of water, a common contaminant in captured carbon dioxide.[7] In terms of epoxides, the majority of studies apply cyclohexene oxide (CHO) or propylene oxide (PO),[2b,d,8] both of which are usually derived by oxidation of petrochemicals. There remains just a single report of the application of a renewable epoxide, limonene oxide, to produce a fully renewable polycarbonate.[9] It is worth also mentioning that even since 1970, many groups have investigated protected glycidyl ethers, which could, in principle, be derived from glycerol.[10]

Epoxides are also applied in ROCOP with anhydrides, utilizing similar catalysts as for epoxide/CO_2 ROCOP.[11] This allows the production of polyesters and, in particular, is an attractive controlled polymerization route to semi-aromatic polyesters with improved thermal properties (*i.e.* higher glass transition temperatures).[11f] Various authors have reported the ROCOP using anhydrides from renewable resources, including maleic or succinic anhydride.[11b,d,f,g,12] Furthermore, phthalic anhydride, which is particularly attractive as it yields thermally resistant aromatic moieties in the polymer backbone, can be produced from carbohydrate derived biomass.[13] In terms of epoxides, so far the only renewable options reported for this ROCOP are limonene oxide and pinene oxide.[11g,12a]

Thus, there is an impetus to consider routes to prepare epoxides from renewable resources as this will allow the production of 100% renewable polyesters/carbonates and is furthermore expected to expand the property profiles for this class of material. In this context, plant oils are an interesting feedstock, as they are produced on sufficient scale and at relatively low cost. Already today, they are used as biofuels and as a source of renewable monomers.[14] A range of transformations of such triglycerides and fatty acids, including polymerizations, have already been reported.[15] Of these methods, olefin metathesis is particularly interesting, as it can be used to produce long-chain carboxylic acids/esters.[16] These are interesting monomers to produce materials with properties approaching some of those of polyethylene.[17] *Inter alia*, during oleochemical olefin metathesis reactions, a common by-product is 1,4-cyclohexadiene (CHD), if polyunsaturated fatty acids (*i.e.* linoleic and/or linolenic acid) are present in the fatty acid mixture.[18] For instance, the self-metathesis of polyunsaturated fatty acid methyl esters was used to prepare long-chain diesters, which are important AA-type monomers.[17b,19] In these metathesis processes, CHD is obtained as a waste by-product, as recently reported by Meier *et al.*[20] Cole-Hamilton and co-workers reported the metathesis of cardanol and ethylene, also yielding CHD as a by-product,[21] offering an alternative route to renewable CHD. In this context, the valorisation of CHD would be particularly beneficial to the biorefinery concept, where all products of a feedstock should be utilized. Recently, Meier *et al.* described the synthesis of substituted caprolactones and their polymers, prepared *via* the modification of cyclohex-2-en-1-one, which was obtained from CHD.[22] Moreover, 1,3-cyclohexadiene, obtained *via* isomerization of CHD, can directly be used in polymerization reactions involving anionic, cationic, and free-radical mechanisms.[23] The poly(cyclohexadiene)s are of interest, since these polymers display good properties and can be transformed into conducting polymers and proton conductors.[1,24] Mathers and co-workers presented a very attractive strategy using 1,4-CHD, obtained from un-purified plant oils, to prepare poly(cyclohexadiene)s *via* a one- or two-step isomerization polymerization cascade.[25] Here, the strategy to valorise CHD is to investigate its transformation into epoxides and the subsequent ROCOP reactions using these bio-derived epoxides.

Results and discussion

Epoxides from 1,4-cyclohexadiene

Epoxides are interesting and important monomers to prepare polycarbonates or polyesters by ROCOP methods. Given the widespread application of cyclohexene oxide (CHO) in ROCOP polymerizations, CHD should be a promising substrate to produce both new and known materials that are fully renewable. We observed that CHD can be converted into various epoxides, including 4,5-epoxycyclohex-1-ene (cyclohexadiene oxide **1** = CHDO), cyclohexene oxide (CHO, **2**) and two diastereomeric bis-epoxides (**3a**, **3b**) using the reagents and conditions shown in Fig. 1.

The oxidation of CHD was accomplished using *meta*-chloroperbenzoic acid (*m*CPBA),[26] in dichloromethane at 298 K, to yield monomer **1** in 82% yield. Alternatively, a more sustainable oxidation of CHD was successfully performed using Oxone® leading to the production of **1** in 65% yield. Interestingly, cyclohexene oxide (CHO) **2** was also prepared from CHD by a selective bi-phasic hydrogenation leading to cyclohexene, and its subsequent oxidation.[27] For the hydrogenation reaction using **1**, the use of Pd/C under 1 atm of H_2 was unsuccessful, but the use of Pd/C(en),[28] in THF under 1 atm of H_2 for 24 h, enabled formation of CHO, together with the formation of side-products such as, among others, the corresponding vicinal diols (as determined by ^{1}H NMR). Thus, this route allows access to CHO from renewable resources as an alternative to the more usual routes to petrochemicals (from benzene).

Finally, in order to explore the range of epoxides accessible from CHD, a complete oxidation of **1** to the bis-epoxides **3a** and **3b** was investigated. Thus, the oxidation of **1** was performed using a slight excess of *m*CPBA (1.05 equivalents per double bond) at 298 K in dichloromethane to yield the corresponding bis-epoxides (**3a** (20%), **3b** (65%)). Alternatively, Oxone can also be used as the oxidant leading to variable

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proportions of the bis-epoxides (depending on the quantity of Oxone® applied, for more details see ESI†).

ROCOP using bio-derived epoxides

The bio-derived epoxides were applied in ROCOP reactions, using either CO_2 or phthalic anhydride as a co-monomer. These polymerizations all require catalysts; four different homogeneous catalysts with a good track record in these fields were compared (the structures of which are illustrated in Fig. 2 and 3).[7a,11c,12b,29]

ROCOP using monomer **1**, catalysed by the di-zinc complex **C1**, did not result in polymer formation, even under the conditions previously successfully used for the ROCOP of CHO (80 °C, atmospheric CO_2 pressure). Increasing the temperature to 100 °C led to some formation of the cyclic carbonate, but no polymer. These results prompted us to investigate the magnesium analogue **C2**, which had previously been found to be both more active and more selective than **C1**.[7a] Thus, ROCOP using **1**, catalysed by **C2** (0.2 mol%) under atmospheric CO_2 pressure, afforded well-defined, perfectly alternating polycarbonates (*i.e.* no formation of ether linkages or cyclic carbonate was observed (see Fig. S3†), albeit with considerably lower activity than the analogous copolymerizations using **2**.[7a] The

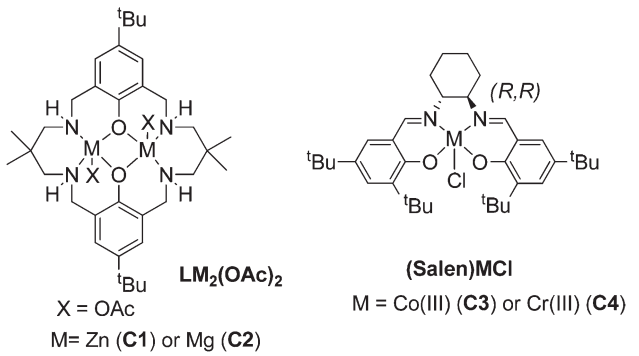

Fig. 2 Structures of the four homogeneous catalysts investigated for ROCOP (for catalyst synthesis methods, see the ESI†).[7a,11c,12b,29]

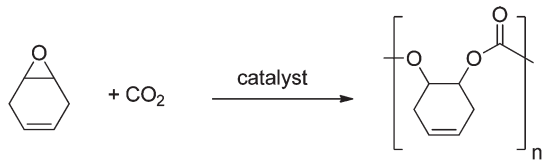

Fig. 3 ROCOP of monomer **1** utilizing catalysts **C1**–**C3**. Catalyst **C3** was applied in combination with a co-catalyst (PPN-Cl).

^{1}H NMR spectrum of the crude product (Fig. S2†) was used to determine the monomer conversion; specifically this was achieved by comparison of the relative, normalized integrals for the cyclohexyl resonances (3.24 ppm **1**, 4.96 ppm polymer) and for the olefin signals (5.43 ppm **1**, 5.57 ppm polymer). In both cases, the same conversions were obtained, suggesting that the double bond was unreactive and that there was no formation of cross-linked polymers. In addition, monitoring the reaction by *in situ* ATR-IR spectroscopy using **1** showed linear formation of the polymer with time, in accordance with results previously obtained with **C1** for CHO/CO_2 copolymerization (see Fig. S4†).[7b] Gel permeation chromatography (GPC) analysis of the polymers exhibited molecular weight distributions with a small shoulder to higher molecular weights (see Fig. S5†), similar to previous obtained ROCOP results using these types of catalysts.[7b] The structure of the polymers was confirmed by MALDI-ToF mass spectrometry. The MALDI-ToF spectrum (see ESI, Fig. S6†) exhibited two series of chains, corresponding to chains end-capped with α-acetate-ω-hydroxyl and α,ω-dihydroxyl moieties.

In order to further investigate the reactivity of **1** in ROCOP, a well-known CHO/CO_2 catalyst, (1*R*,2*R*)SalcyCo(III)-Cl complex **C3**, was applied. Thus, the ROCOP using **1**, catalysed by **C3** (0.2 mol%) and with PPN-Cl (0.2 mol%) as co-catalyst, under 20 bar CO_2 pressure, also afforded polycarbonate without formation of any cyclic carbonate or ether linkages, albeit once again with a lower turn-over frequency than the analogous polymerizations using **2**.[12b] In addition, the ^{1}H NMR spectra of both the crude and purified polymer showed that the double bond remains unreacted after polymerization, allowing access to unsaturated CO_2-derived polycarbonates. The polymers prepared using the cobalt catalyst showed slightly higher molecular weights (12.9 kg mol^{-1}), bimodal molecular weight distributions and narrow dispersities (1.18) (see Fig. S7†). Furthermore, ROCOP occurred in a controlled manner, as evidenced by a linear correlation between the monomer conversion and the polymer molecular weight (see ESI, Fig. S8†).

Thus, applying a range of different copolymerization catalysts (**C2**, **C3**) enabled the successful copolymerization of **1**/CO_2, although the rates were lower than the analogous polymerizations run using cyclohexene oxide **2**/CO_2.[7a,12b,29] This likely relates to different metal binding energies of the two epoxides.

Terpolymerizations of **1**/CHO/CO_2 were also investigated (Fig. 4); the incorporation of **1** was attractive as a means to introduce unsaturation into the polymer backbone, allowing for further post-polymerization modifications.[30] Different cata-

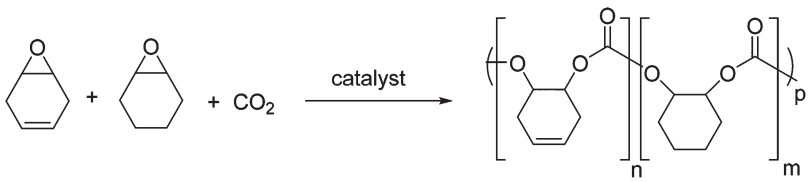

Fig. 4 The terpolymerizations of **1**, CHO and CO_2 so as to produce partially unsaturated polycarbonates.

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Table 1 Shows the results of ROCOP using monomer **1**

Polymer	Catalyst	Co-Cat.	CO_2 [bar]	[M] : [Cat.]	T [°C]	Conv. [d] [%]	TOF [h^{-1}]	M_n [e] [kg mol^{-1}]	$Đ$
P1	**C1**	—	1	500 : 1	80	0	—	—	—
P2[a]	**C1**	—	1	500 : 1	100	12	4	—	—
P3	**C2**	—	1	500 : 1	80	25	5	2.9	1.17
P4	**C2**	—	1	250 : 1	80	20	3	2.5	1.08
P5	**C2**	—	1	500 : 1	100	21	6	2.8	1.15
P6	**C3**	—	20	200 : 1	20	15	1	5.3	1.43
P7	**C3**	PPN-Cl	20	500 : 1	28	78	65	12.9	1.18
P8[b]	**C2**	—	1	500 : 1	80	(11/56)[b]	21	4.0	1.15
P9[c]	**C3**	PPN-Cl	20	500 : 1	28	(22/72)[c]	118	11.5	1.12

[a] The only product of this reaction was cyclic carbonate. [b] Mixtures of monomers **1** and **2** were applied such that the ratio of **1** : **2** was 4 : 1 and the conversion is given for the respective monomer. [c] Mixtures of monomers **1** and **2** were applied such that the ratio of **1** : **2** was 1 : 1 and the conversion is given for the respective monomer. [d] Conversion was determined by ^{1}H-NMR spectrum of the crude product by comparison of the relative normalized integrals for the cyclohexyl resonances (3.24 ppm **1**, 4.96 ppm polymer) and for the olefin signals (5.43 ppm **1** and 5.57 ppm polymer). [e] Molecular weights and polymer dispersities were determined by GPC calibrated with polystyrene standards.

lysts and ratios of monomers **1** : **2** were investigated (see Table 1). The relative monomer conversions were determined by ^{1}H NMR spectroscopy by integrating the signals of the cyclohexyl moiety in the polymer (4.96 ppm for incorporated **1**, 4.66 ppm for incorporated **2**) and monomer (3.24 ppm **1**, 3.11 ppm **2**), respectively. Once again, the terpolymerizations using di-magnesium **C2** are significantly slower than those with the cobalt salen complex **C3**. GPC analysis revealed polycarbonates with moderate molecular weights of (4–11.5 kg mol^{-1}) and narrow dispersities (<1.15).

Finally, the bis-epoxides **3a** and **3b** were selected to prepare branched or cross-linked polycarbonates, however, in all cases completely insoluble material was produced which limited further analysis but was indicative of the formation of cross-linked products.

Unsaturated polyesters by ROCOP

Monomer **1** was also used for the synthesis of unsaturated polyesters *via* ROCOP with phthalic anhydride (Fig. 5). An attractive feature of the products would be the facility to introduce unsaturation into the polymer backbone. It is notable, that many researchers have reported problems in copolymerizing maleic anhydride (a similarly unsaturated co-monomer) and thus novel routes to unsaturated polyesters are of interest.[11c,12b]

Catalyst **C1** did not afford any polymerization, whereas **C2** enabled the slow formation of perfectly alternating polyesters. Similarly, catalysts **C3** and **C4** were effective and yielded unsaturated polyester. In each case, the monomer conversion was estimated using ^{1}H NMR spectroscopy. In particular, the relative integrals were compared for the aromatic signals (for PA at 7.81–7.67 ppm and for polymer at 7.66–7.36 ppm, see Fig. S11,† Table 2). Utilizing the salen based catalysts yielded polyesters of moderate molecular weights (7.5 kg mol^{-1}) and narrow dispersities (1.20) with TOF values up to 246 h^{-1}. The chromium salen catalyst (**C4**) showed the best performance at a reaction temperature of 110 °C in presence of PPN-Cl as co-catalyst. Polymerizations in bulk were hampered by viscosity

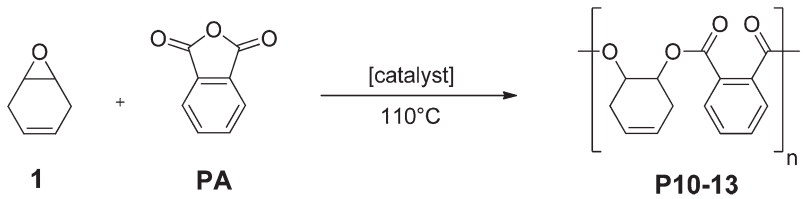

Fig. 5 ROCOP using epoxide **1** and phthalic anhydride (**PA**).

Table 2 Results of the co-polymerization of monomer **1** and phthalic anhydride (**PA**)

Polymer	Catalyst	[**1**] : [**PA**] : [Cat.]	T [°C]	Conv. [c] [%]	TOF	M_n [d] [kg mol^{-1}]	$Đ$
P10[a]	**C2**	250 : 250 : 1	120	10	6.25	1.6	1.18
P11	**C3**	250 : 250 : 1	110	48	60	4.3	1.23
P12	**C4**	250 : 250 : 1	110	74	246	4.5	1.34
P13[b]	**C4**	250 : 250 : 1	110	91	75.8	7.5	1.17

[a] Reaction was performed without co-catalyst. [b] Reaction was conducted in toluene (2.5 M). [c] Conversion was determined from the ^{1}H-NMR spectrum of the crude product by comparison of the relative, normalized integrals for the cyclohexyl resonances (4.96 ppm polymer, 4.64 ppm polymer, 3.24 ppm **1**, 3.11 ppm **2**). [d] Molecular weights and polymer dispersities were determined by GPC calibrated with polystyrene standards.

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Table 3 Shows the results of the thermal analysis of the polycarbonates

Polymer		M_n (PDI) (kg mol^{-1})	T_d [a] [°C]	T_g [a] [°C]
P7	**1**/CO_2	12.9(1.18)	255	115
P9	CHO/**1**/CO_2	11.5 (1.12)	285	112
P13	**1**/PA	7.5 (1.17)	325	128

[a] Representative DSC and TGA figures are included in the ESI.

increases; however, using monomer solutions (2.5 M in toluene) led to conversions of 91% within 3 h. ROCOP occurred in a controlled manner, as evidenced by a linear correlation between the monomer conversion and the polymer molecular weight (see Fig. S13†). Interestingly, for both **C3** and **C4**, the use of PPN-Cl as the co-catalyst was required to increase the activity. It is notable that compared to maleic anhydride/epoxide copolymerization, where the co-catalyst was purported to react with the olefin moiety,[12b] in this case the double bonds remained unreacted in the polymer.

Thermal properties of polyesters and polycarbonates

The thermal properties of the unsaturated polycarbonates were studied by TGA and DSC analysis (Table 3). The polycarbonates prepared from **1** showed glass-transition temperatures of approximately 115 °C (depending on the molecular weight), a value close to that reported for PCHC (polycyclohexene carbonate, the polymer produced by copolymerization of **2**/CO_2).[1,31] The thermal degradation temperature (10% weight loss) of **P7** was 255 °C, whereas that of **P9** was higher at 285 °C. Both values are somewhat lower than that reported for poly(cyclohexene carbonate) ($T_d \sim 300$ °C [32]), suggesting that the olefin group slightly lowers the thermal stability. Terpolymers, especially **P8** (T_g = 106 °C), showed slightly lower glass transition temperatures than PCHC or **P3**–**P7** (T_g = 115 °C), which is mainly due to the low molecular weight of **P8**. The thermal properties of the polyesters derived from **2**/phthalic anhydride showed better thermal properties, with glass transition temperature of 128 °C and a thermal decomposition temperature (10% weight loss) of 325 °C. It is noteworthy that polyesters derived from CHO/phthalic anhydride typically show a T_g below 100 °C.[11e,29]

Conclusions

The preparation of a series of epoxides from 1,4-cyclohexadiene, which is itself a by-product of the self-metathesis of triglycerides and other fatty acid derivatives, are presented. The diene was epoxidized, using various oxidants, to yield cyclohexadiene oxide or a bis-epoxide product. The diene could also be partially hydrogenated to cyclohexene and then oxidized to yield the well-known monomer cyclohexene oxide. The development of a bio-derived route to cyclohexene oxide is of interest, as the monomer is widely applied in various ring-opening copolymerization reactions, including epoxide/CO_2 to produce polycarbonates or epoxide/anhydride to produce polyesters. Thus, the method presented here provides an alternative route to prepare cyclohexene oxide.

Furthermore, the preparation of the bio-derived, unsaturated epoxide is also of high interest as it enables the preparation of partially unsaturated polycarbonates and polyesters. For the co-polymerization with CO_2 and cyclohexadiene oxide, the readily available cobalt salen complex provided the best results and yielded a polycarbonate with closely related thermal properties to the well-known poly(cyclohexene carbonate). Terpolymerizations of CO_2, cyclohexene oxide, and cyclohexadiene oxide were also successful yielding polycarbonates with controllable quantities of unsaturation. Copolymerization of cyclohexadiene oxide and phthalic anhydride leads to renewable, unsaturated polyesters having high glass-transition and decomposition temperatures. These unsaturated polycarbonates and polyesters offer the possibility for further modification of the double bond, which would be expected to alter the polymer properties. Future research will focus on further development of the synthesis of epoxides from biomass as well as the post-polymerization functionalization and application of such unsaturated polyesters and polycarbonates.

Acknowledgements

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