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Ring opening metathesis polymerisation of a new bio-derived monomer from itaconic anhydride and furfuryl alcohol†

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A new oxa-norbornene bio-based lactone obtained from the 100% atom economic reaction of furfuryl alcohol and itaconic anhydride *via* a tandem Diels–Alder addition and lactonisation is presented. Esterification of the resulting acid gives a monomer for the production of a bio-based polymer with low polydispersity and well controlled molecular weight *via* ring-opening metathesis polymerisation (ROMP).

Introduction

The development of novel functionalised bio-based molecules *via* facile, green synthetic routes is a major challenge of modern synthetic chemistry. There is interest in the use of furan-based compounds for the development of platform molecules and polymers due to their aromatic and dienic character, large structural variation and their easy accessibility from renewable resources.[1,2] Furfural (2-furancarboxyaldehyde) is industrially produced (*ca* 200 000 tons per year) by the acid-catalysed dehydration of pentoses, with some being subsequently reduced to furfuryl alcohol **1**. However, these compounds can be unstable due to uncontrolled self-condensation reactions occurring in the presence of acids or heat. Itaconic acid is another bio-derived platform molecule with growing prevalence in the field of polymer synthesis and is particularly interesting due to its functionality, containing both a dicarboxylic acid and a carbon–carbon double bond.[3–6] Production of itaconic acid by the fungal fermentation of glucose using *Aspergillus terreus* is predicted to grow to 400 000 tons per year by 2020.[7–9] Radical polymerisation of itaconic acid and many of its esters is well known. However, as homopolymers the glass transition temperatures (T_g) of poly(itaconate alkyl esters) are often below room temperature,[10,11] limiting their usefulness for many applications. To alleviate this problem copolymers of these monomers with conventional acrylates are often prepared.[12,13] Poly(itaconic acid) and its salts are useful hydrophilic materials in commercial absorbents, as a co-monomer for styrene–butadiene rubber latexes, and in chelating agents.[8] Unsurprisingly, the diacid functionality of itaconic acid, or its corresponding anhydride, has been used to make polyesters.[14–16] However, few groups have studied the functionalisation of itaconic acid with more complex bio-based compounds, particularly furanic structures. This opens up the possibility for the development of new interesting fully bio-derived functionalised monomers and polymers.

Results and discussion

As benzylic and other aromatic itaconate esters are known to produce polymers with higher T_g than their alkyl equivalents,[17] we attempted to synthesise a bio-derived analogue of these by preparing itaconate esters with furfuryl alcohol **1**. However, when **1** was reacted with itaconic anhydride **2** (Scheme 1), at room temperature in acetonitrile solution for 24 hours, a crystalline solid formed that proved to be a novel oxa-norbornene structure **5** (61%), generated *via* a 100% atom economical tandem ring-opening and Diels–Alder addition, rather than the expected mono-esters **3a** or **3b**.

Although extensive work has previously been conducted on the reaction of maleic anhydride and furan derivatives, particularly for the formation of phthalic anhydrides *via* Diels–Alder addition and dehydration,[18–20] the reaction of **1** and **2** has not, to our knowledge, previously been studied.

Further tests showed that the reaction also occurred in the absence of solvent (68%), with the product **5** still precipitating

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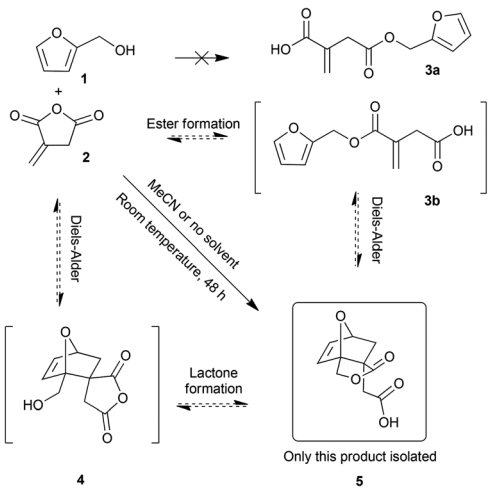


Scheme 1 Preparation of oxanorbornene–lactone monomer 5 *via* one-pot, tandem Diels–Alder and lactonisation reactions.

direct from the neat reaction mixture. If necessary, the crude product can be recrystallized from acetone or ethanol. Acid **5** was found to be extremely stable, showing no degradation over several weeks when stored under ambient conditions.

Analysis of the product by NMR spectroscopy clearly showed that the intended mono-ester **3a** was absent, as were starting materials **1** and **2**. However, both mass spectrometry and elemental analysis showed the product formed had the same molecular formula as **3a** and **3b**, leading us to consider other potential addition reactions.

Furans are well known dienes for Diels–Alder additions, including the reaction of maleic anhydride with **1**.[18,19,21] Therefore, a combined Diels–Alder addition and ring-opening reaction to form tricyclic acid **5** was predicted to have occurred (Fig. S1†) and was shown to fit the observed spectroscopic data. Detailed analysis by NMR spectroscopy of the crude, purified and recrystallised products indicated the formation of a single isomer (*exo*), with only minor by-products attributed to polymerised furfuryl alcohol. Single crystal X-ray diffraction unambiguously identified the product as **5** (Fig. 1).‡ The mechanism of this reaction is more interesting than it appears at first glance. Previous studies show that the reaction of itaconic anhydride with an alcohol regioselectively gives the ester furthest from the alkene functionality, in this case ester **3a**.[22–24] However, the lactone present in **5** is the result of the esterification occurring at the carboxylic acid group adjacent to the alkene.

Presently it is not known whether the esterification reaction precedes the Diels–Alder cycloaddition, yielding intermediate **3b**, or whether the Diels–Alder cycloaddition occurs first, giving intermediate **4**, followed by the formation of a cyclic lactone **5**. A preliminary kinetic study proved inconclusive as neither of intermediates **3b** or **4** were observed as the reaction progressed. It would therefore seem likely that the driving force for the observed selectivity must be the crystallisation of this specific isomer from the reaction mixture. Interestingly, the formation of the intermolecular Diels–Alder adduct between maleic anhydride and various furfuryl alcohols to give an oxa-bicyclic product occurs under similar conditions to those used in this reaction.[18] However, the retro-Diels–Alder addition is facile at elevated temperatures or under acidic conditions and the concurrent ring-opening of the anhydride requires either the addition of moisture or a multi-day reaction.[18,21] In some instances oxa-norbornene derivatives are known to autoaromatise *via* elimination of water, though this is not possible in the case of compound **5** due to the presence of tetrasubstitued carbon atoms within the six-membered ring.

Oxa-norbornene derivatives formed from intramolecular Diels–Alder reactions of furans are known to be valuable intermediates for the production of biologically active compounds.[25–29] Crucially, however, oxa-norbornenes are also capable of undergoing ring-opening metathesis polymerisation (ROMP). As obtained, acid **5** did not undergo ROMP in THF using any of the commercially available Grubbs catalysts (1st, 2nd or 3rd generations). Hence, protection of the carboxylic acid was carried out *via* esterification with methanol to give ester **6** (Scheme 2), with the product being purified *via* solvent extraction with water and either dichloromethane (77% yield) or ethyl acetate (62%).

While Grubbs 1st generation catalyst was again found to be inactive when using **6**, the polymerisation did proceed successfully in dichloroethane (DCE) using both Grubbs 2nd generation and Hoveyda–Grubbs catalysts (H-G) (Scheme 3). To the best of our knowledge this is the first reported case of ROMP on a norbornene or oxa-norbornene molecule of this class where the bridgehead is substituted.

Although homopolymerisation of monomer **6** occurred successfully under homogeneous conditions in DCE, with nearly full conversion, the polymer obtained (**7**) after end-capping with ethyl vinyl ether was insoluble in all solvents tested.

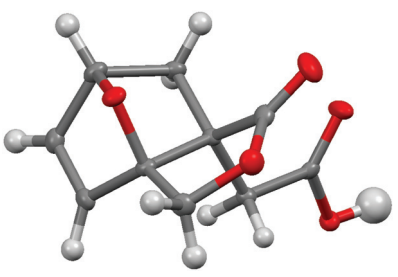
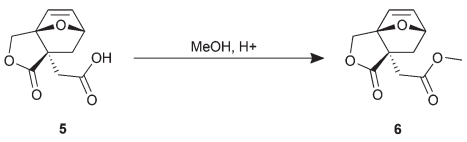
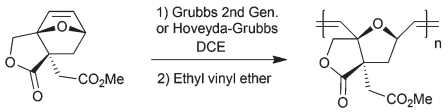


Fig. 1 Single crystal X-ray structure of the isolated oxa-norbornene acid 5.

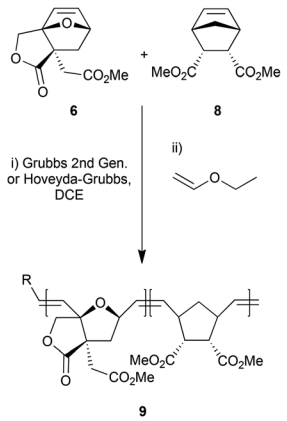


Scheme 2 Esterification of 5 with methanol to produce ROMP monomer 6.



6 7

Scheme 3 ROMP of ester 6 to give homopolymer 7.



6 8 9

Scheme 4 ROMP of monomer 6 and norbornene 8 to give copolymer 9.

Differential scanning calorimetry (DSC) analysis of 7 gave no detectable T_g while the temperature of 10% decomposition (TD_{10}) was determined as 358 °C (Fig. S10†). To address the issue of solubility, copolymerisation of monomer **6** and commercially available dimethyl *endo-cis*-5-norbornene-2,3-dicarboxylate **8** was investigated and resulted in the formation of a soluble copolymers (Scheme 4). As the solubility of this copolymer hinges on the content of comonomer **8** it was subsequently established that a minimum content of 10 wt% is required to afford good solubility to the copolymer.

After polymerization, the fused lactone ring of **6** remained intact as elucidated by DRIFT and NMR spectroscopy.

GPC analysis showed that the soluble random copolymers have narrow molecular weight distributions indicative of a well-controlled polymerization process (see Table 1). As shown in Fig. 2, there was a linear relationship between the copolymer molecular weight and the [catalyst]/[monomer] ratio which is denotive of a living polymerisation. DSC revealed that the polymers were amorphous and had glass transition temperatures ranging from 158 to 163 °C, while STA gave a TD_{10} of 370 °C (Fig. S10†).

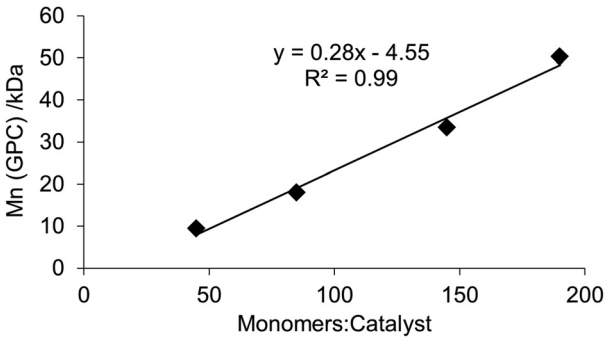


Fig. 2 Plot of the molecular weight *versus* the [monomers]/[catalyst] ratio for copolymers of 6 and 8.

Although DCE has been a common solvent for this type of polymerisation, its current classification by sections of industry as highly hazardous and under REACH as a substance of very high concern makes future use as an industrial solvent very unlikely. Therefore, ROMP of monomer **6** was attempted using dimethyl carbonate (DMC), diethyl carbonate (DEC), tetrahydrofuran (THF) and ethyl acetate as the solvent. 2-Methyltetrahydrofuran, which is derivable from hemicellulose, was also investigated but proved to be a poor solvent for the monomer. As for the materials made in DCE, homopolymers prepared in these solvents were insoluble, therefore 50 : 50 copolymers were prepared. In each case, the molecular weight was very low (Table 2), with the partially formed polymer preci-

Table 2 Molecular weights obtained for preparation of copolymer 9 in various solvents

Solvent	M_n	M_w	PDI
Calculated	21 700	—	1
DCE	21 500	23 700	1.11
Ethyl acetate	2300	2400	1.08
THF	3600	5100	1.40
DMC	4100	5600	1.40
DEC	8600	9700	1.12
DEC[a]	14 200	15 700	1.11

The polymerization using a 50 : 50 : 1 molar ratio of monomers **6** : **8** : Grubbs 2nd generation catalyst was carried out at room temperature for 24 hours, molecular weights were obtained by GPC in THF at 25 °C and calibrated relative to polystyrene standards. [a] Reaction time extended to 72 hours.

Table 1 Molecular weight and thermal analysis of random copolymers 9

[6]:[8]:[i]	Reaction time (h)	Conv.%	$M_{n(calc.)}$	$M_{n(GPC)}$	$M_{w(GPC)}$	PDI	T_g
25 : 25 : 1	16	100	10 850	9500	11 000	1.15	158
50 : 50 : 1	24	100	21 700	21 500	23 700	1.11	159
100 : 100 : 1	48	97	42 000	45 200	53 200	1.17	161
200 : 200 : 1[a]	48	95	82 500	63 200	80 800	1.27	163

The polymerization was carried out in 1,2-dichloroethane at room temperature, GPC was carried out in THF at 25 °C and calibrated relative to polystyrene standards. [a] Reaction temperature 40 °C.

pitating from solution in both ethyl acetate and THF. In DMC the polymer remained in solution during the reaction but only low molecular weight material (M_n = 4000 g mol^{-1}) was obtained. Results in DEC were somewhat more favourable, with the polymer reaching an M_n of 8500 g mol^{-1}, while extending the reaction time to 72 hours increased this further to 14 200 g mol^{-1}. These results indicate that the carbonate solvent is likely coordinating to the ruthenium atom of the catalyst and slowing the rate of reaction relative to DCE.

Conclusions

In this work we have demonstrated the unusual, 100% atom economic, tandem Diels–Alder cycloaddition and lactonisation reaction between itaconic anhydride **1** and furfuryl alcohol **2** to a versatile fused-ring oxa-norbornene derivative **5**. Moreover as itaconic acid and furfuryl alcohol are regarded as key platform molecules for the future bio-based chemical economy, this molecule can be considered fully bio-derivable. Additionally it is shown that the methyl ester **6** readily undergoes ROMP to produce a fully bio-derived and novel polymer, and can form copolymers with other suitable ROMP monomers.

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Notes and references

‡Crystallographic data for compound **5** has been submitted to CCDC and given code CCDC 1454993. All data used in the preparation of this manuscript is contained within this document, the ESI or available *via* a depository (DOI: 10.15124ee9b6f2f-1409-4343-b855-bd5af8d97bc7).

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