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Rapid ring-opening metathesis polymerization of monomers obtained from biomass derived furfuryl amines and maleic anhydride

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Abstract: Well-controlled and extremely rapid ring-opening metathesis polymerization of unusual oxa-norbornene lactam esters by Grubbs 3rd generation catalyst is used to prepare a range of bio-based homo- and co-polymers. Bio-derived oxa-norbornene lactam monomers were prepared at room-temperature from maleic anhydride and secondary furfuryl amines using a 100% atom economical, tandem Diels-Alder-lactamization reaction, followed by esterification. Several of the resulting homo- and co-polymers show good control over polymer molecular weight and have narrow molecular weight distributions.

Introduction

At present, the polymer industry is the largest consumer of petrochemical resources after fuels, using around 4% of global oil to produce the vast majority of the 300 million metric tonnes of new plastic made each year.^[1] Plastics are integral to modern life, and are used in packaging, consumer products and technology applications for which competing non-plastic alternatives are unattractive. Clearly, therefore, any future bio-based chemical economy will have to address the need for new bio-derived polymers to fill this demand based upon feedstocks that are available without competition with food and at significant scale.

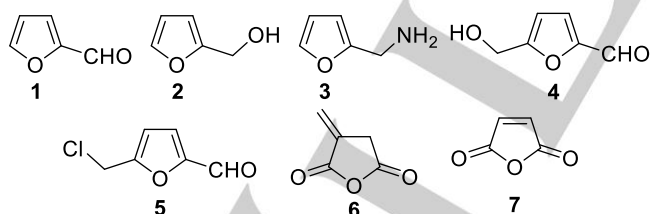
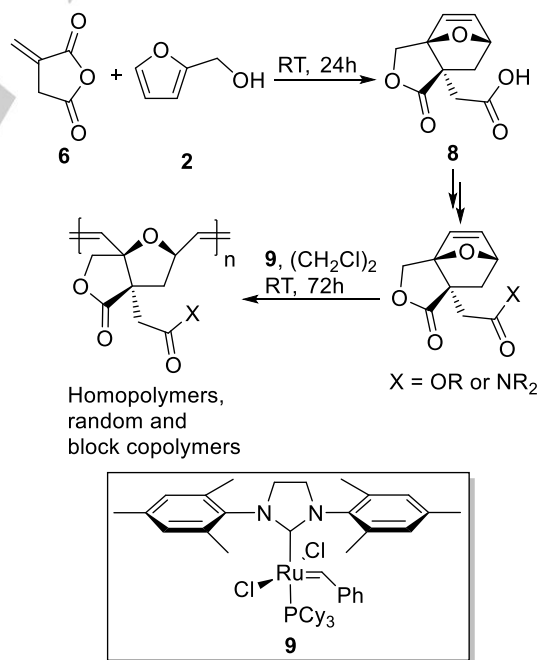


Figure 1: Structures of furan derivatives 1-5 and anhydrides 6-7.

Furfural **1** (Figure 1) has been produced on a scale of hundreds of thousands of tonnes per year from agricultural waste for many years^[2] and is readily converted to furfuryl alcohol **2**^[3] and furfurylamine **3**.^[4] Related furan derivatives such as hydroxymethyl furfural **4** and chloromethyl furfural **5** are widely recognized as being key platform molecules as they are obtainable at scale from waste biomass and retain a great deal of chemical versatility.^[5] Itaconic anhydride **6** is readily obtained directly from citric acid by reactive distillation, the citric acid itself being producible by fermentation,^[6] whilst maleic anhydride **7** can be made catalytically from either **1**,^[7] or **4**.^[8] Maleic anhydride already finds large scale and widespread use in the polymer, pharmaceutical, and agrichemical industries,^[9] which implies that the production of bio-based maleic anhydride will be important in the future, allowing this feedstock to benefit from the corresponding economies of scale.



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Supporting information for this article is given via a link at the end of the document.

Scheme 1: Prior work on ROMP of fully bio-based monomers prepared from itaconic anhydride.

Furans are known to undergo rapid and reversible Diels-Alder reactions with a variety of dienophiles, including maleic anhydride.^[10] In recent work, we were able to demonstrate that the reaction between itaconic anhydride **6** and furfuryl alcohol **4**

proceeded cleanly at room temperature to give acid **8** by a one-pot and 100% atom-economical tandem Diels-Alder-lactone formation process requiring no additional reagents, catalysts, or solvents (Scheme 1).^[11] The same result was obtained independently and simultaneously by the group of Hoyer.^[12] We also demonstrated that a variety of esters and amides of acid **8** are good substrates for ring-opening metathesis polymerization (ROMP) using Grubbs second-generation catalyst **9**. The polymerizations displayed a well-controlled linear relationship between polymer molecular weight and monomer:catalyst ratio and were able to produce both random and block copolymers.^[13] However, the polymerization of these monomers was very slow, with a typical reaction taking 72 hours to reach completion. This limited the variety of polymer architectures which could be produced as “dead” chain ends become a significant problem over extended polymerisations, causing difficulties in forming large block copolymers. From a green chemistry perspective, an additional problem with the polymerization of the monomers shown in Scheme 1 was the need to use dichloroethane as the polymerization solvent.

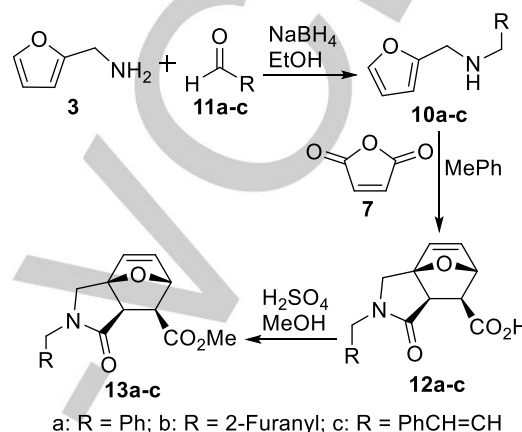
The slow rate of polymerization of monomers derived from acid **8** could, at least in part, be attributed to the presence of a substituent (CH₂COX) in the *endo*-position of the oxanorbornene ring.^[14] Therefore, it was natural to search for other furan derivatives and anhydrides which would also undergo tandem processes involving Diels-Alder reactions, but which would do so to give oxanorbornene adducts with no substituents in the *endo*-positions. Hence, in this study, we report on the use of bio-based furfuryl secondary amines in place of furfuryl alcohol, and the use of bio-derivable maleic anhydride in place of itaconic anhydride. The resulting bio-based monomers, are shown to undergo well-controlled and rapid ROMP to give homo- and co-polymers, with reactions typically reaching completion after reaction times of just a few minutes. The rapid rates of polymerization also permitted the use of dimethyl carbonate as a green solvent for the polymerizations.

Some of the homo- and co-polymers prepared in this work contain both furans and alkenes and so have the potential to form self-healing films by reversible Diels-Alder reactions. All of the polymers also have the ability to undergo post-polymerization modification by treatment with thiols and end-group modification.^[15] This gives them potential biological applications^[16] and allows their use as functional surfaces and supports.^[17]

Results and Discussion

Three secondary furfuryl amines (**10a-c**) were prepared by the reductive amination of aldehydes **11a-c** with furfurylamine **3** (Scheme 2). Amines **10a-c** then underwent tandem Diels-Alder and lactamization reactions to give acids **12a-c** when treated with maleic anhydride **7**. In contrast to our previously reported synthesis of acid **8**,^[11] it was necessary to use a solvent (toluene) for this reaction due to the viscous nature of amines **10a-c**. In each case, the Diels-Alder product (**12a-c**) precipitated from the reaction mixture and could be further purified by

recrystallization from acetone. The structure and relative configuration of each of acids **12a-c** was confirmed by single crystal X-ray diffraction.^[18] Importantly, these structures confirmed that there had been no epimerization at the carbon adjacent to the carboxylic acid and hence that all of the substituents were on the *exo*-face of the oxanorbornene ring. Carboxylic acids **12a-c** were converted into the corresponding methyl esters (**13a-c**) by an acid-catalysed esterification.

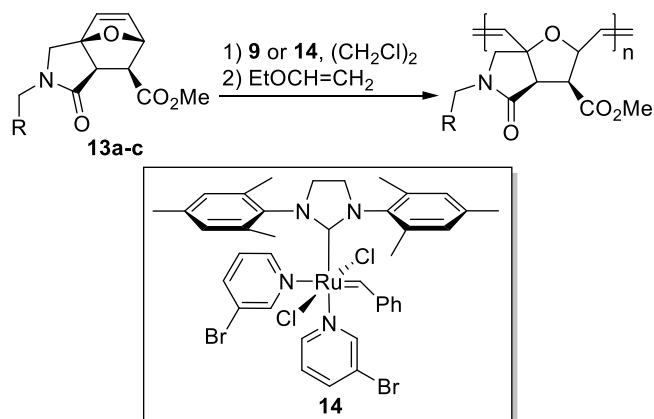


Scheme 2: Synthesis of monomers **13a-c**.

ROMP of esters **13a-c** with Grubbs second generation catalyst **9** was found to be possible, but not well controlled, giving relatively broad molecular weight distributions from reactions carried out for 72 hours under similar conditions to our prior work (Scheme 3). This was initially thought to be a consequence of unwanted back-biting or intermolecular metathesis side reactions, and therefore the influence of reaction time on degree of polymerization was investigated. As a result, it became apparent that monomers **13a-c** polymerized at a rate many times greater than previously observed for the esters or amides of acid **8** with reactions monitored by ¹H NMR spectroscopy reaching completion in minutes instead of days.^[11,13,19] Once this was established, it was evident that the cause of the increased polydispersity was that the rate of propagation K_p was rapid relative to the rate of initiation K_i for these monomers using Grubbs second generation catalyst. Therefore, the use of Grubbs 3rd generation catalyst **14** was investigated as it is known to have a very rapid rate of initiation.^[20] As expected, the rate of propagation during polymerizations of monomers **13a-c** was very similar with catalysts **9** and **14**. However, due to the increased rate of initiation, the polydispersity of the polymers was dramatically improved when using catalyst **14**.

The polymerization of benzyl monomer **13a** (100 equivalents of monomer relative to catalyst **14**) was monitored by ¹H NMR spectroscopy and found to reach completion with either catalyst **9** or **14** within 20 minutes. With catalyst **14**, the polymers showed a low dispersity ($\mathcal{D} \leq 1.07$, Table 1) and a linear relationship between molecular weight and monomer:catalyst ratio up to a ratio of at least 500:1 (Table 2

and Figure 2). In contrast, polymers prepared using catalyst **9** had dispersities of 1.28 to 1.53.



Scheme 3: ROMP of monomers **13a-c** with Grubbs catalysts **9** and **14**.

Table 1. Homopolymerization conversion and molecular weight data of monomer **13a** with catalyst **14**.^[a]

Time (min)	% Conversion (¹ H NMR)	M _n (Da)	M _w (Da)	Đ
2	67	26642	27565	1.03
3	74	29715	30965	1.04
4	80	31523	33178	1.05
10	95	38099	40501	1.06
20	99	39840	42473	1.07
30	99	39966	42565	1.07

[a] Reactions carried out in dichloroethane at 25 °C using a 100:1 ratio of monomer **13a** to catalyst **14**.

Monomer **13b** was found to polymerise at a similar rate to **13a** and reactions were again complete in 30 minutes (Table 3 and Figure 3). For both monomers, the rate of polymerization could be determined (Figure 4) and the observed first order rate constants K_{pobs} for the polymerizations of **13a** and **13b** respectively were $4 \times 10^{-3} \text{ s}^{-1}$ and $5 \times 10^{-3} \text{ s}^{-1}$ which are approximately 200 times greater than the previously determined K_{p} for the methyl ester of acid **8** ($2.2 \times 10^{-5} \text{ s}^{-1}$).^[13] This large increase in rate of propagation is entirely consistent with the absence of substituents in the *endo*-positions of monomers **13**.

Table 2. Molecular weight data for the homopolymerization of monomer **13a** at various ratios to catalyst **14**.^[a]

13a:14 ratio	M _n (Da)	M _w (Da)	Đ
25:1	21405	22996	1.07
50:1	36646	39025	1.06
100:1	62537	70149	1.12
200:1	101950	111580	1.09
500:1	260090	273470	1.05

[a] All reactions were carried out at 25 °C in dichloroethane for 20 minutes using a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent). All reactions had gone to completion after 20 minutes.

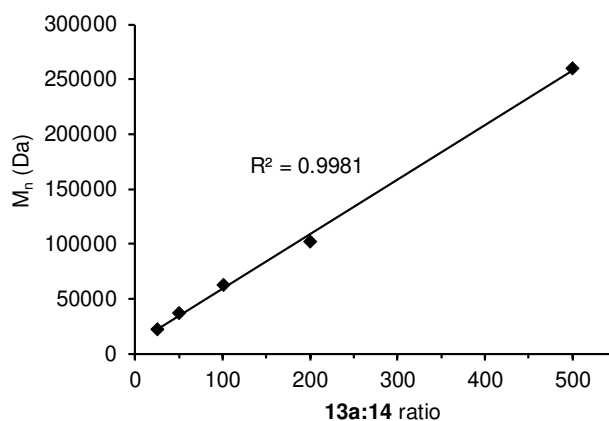


Figure 2: Linear relationship of molecular weight (M_n determined by SEC) and the **13a:14** ratio.

Table 3. Homopolymerization of monomer **13b**.^[a]

Time (min)	Conversion (%)	M _n (Da)	M _w (Da)	Đ
2	61	24190	25475	1.05
4	80	33131	34486	1.04
6	89	36618	38542	1.05
8	93	38332	40788	1.06
10	96	39156	41640	1.06
20	98	40333	43267	1.07
30	100	41301	43873	1.06

[a] All reactions were carried out at 25 °C in dichloroethane using a monomer to catalyst ratio of 100:1 and a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent).

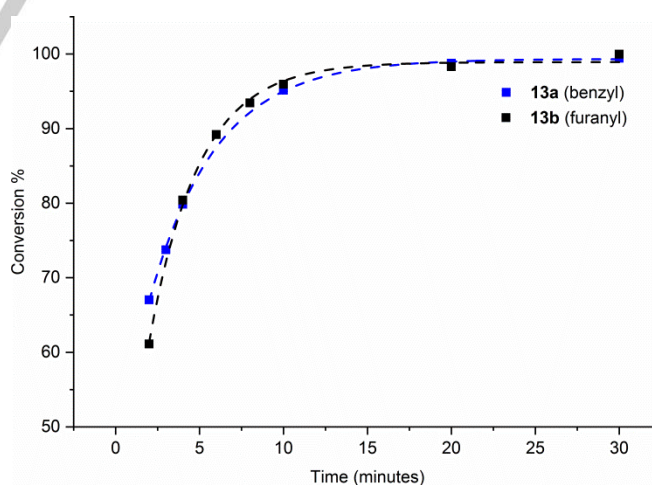


Figure 3: Polymerization of monomers **13a** and **13b** over time. (Dotted lines for illustrative purposes only)

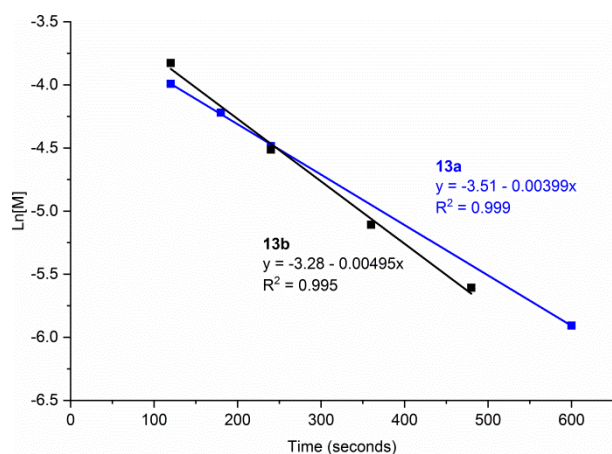


Figure 4: Observed first order kinetics of the homopolymerization of monomers **13a** and **13b**.

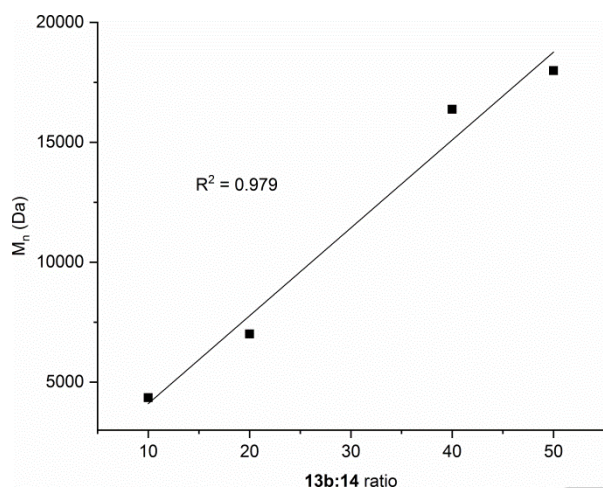


Figure 5: Linear correlation of molecular weight to **13b:14** ratio.

Table 4. Low molecular weight homopolymers at various **13b:14** ratios.^[a]

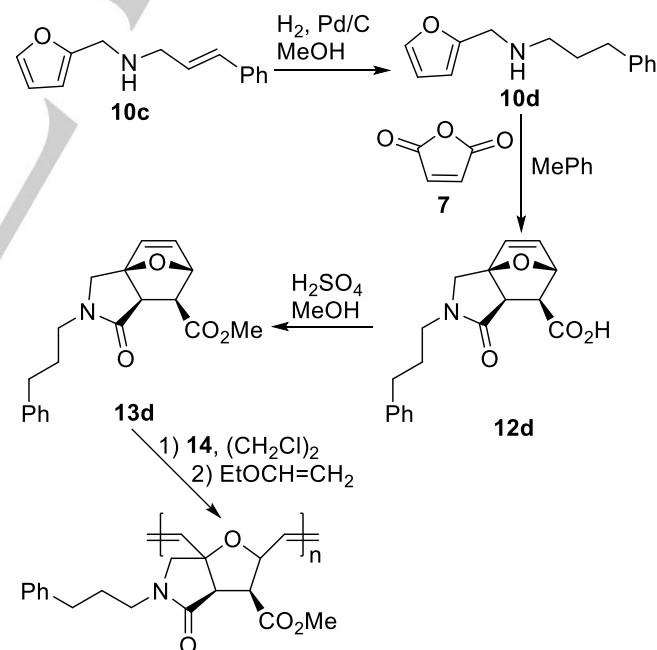
13b:14 ratio	M_n (Da)	M_w (Da)	\bar{D}
10	4350	4782	1.1
20	7010	7402	1.05
40	16377	17434	1.06
50	17991	18611	1.03

[a] All reactions were carried out at 25 °C in dichloroethane for 30 minutes using a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent). All reactions had gone to completion in this time.

Up to a monomer to catalyst ratio of 50:1, there was a linear relationship between the **13b:14** ratio and molecular weight (Figure 5) and the homopolymers had narrow molecular weight distributions (Table 4). However, above a monomer to catalyst ratio of 50:1, homopolymers of monomer **13b** gave bimodal molecular weight distributions by SEC, with the higher

molecular weight polymers (run at higher concentration of monomer) showing this to a greater extent. An explanation of this effect was that the pendant furfuryl groups and the alkenes of the polymer backbone were undergoing a Diels-Alder reaction, causing first chain extension, and then crosslinking. For a **13b:14** ratio of 500:1, the resulting polymer was extremely difficult to filter and formed a swollen gel in THF rather than dissolving, indicating that this material was indeed cross-linked. Shoulders were observed on both the low and high molecular weight sides of SEC peaks, consistent with both intramolecular and intermolecular Diels-Alder reaction occurring. The intermolecular reaction would increase the molecular weight of the polymer, whilst the intramolecular reaction will create looped chains which would appear to have a lower molecular weight by SEC than the corresponding linear polymer. Although the Diels-Alder reaction of the furan with the unstrained backbone alkene is expected to be relatively slow, even <1% of polymer repeat units undergoing inter- or intra-molecular crosslinking during the course of the reaction, or in solution after polymerization, will inevitably lead to dramatic changes in the measured molecular weight distribution.

As Diels-Alder reactions of furans are known to be reversible,^[10] an attempt was made to un-crosslink a sample of 500:1 homopolymer by refluxing it in a large volume of THF. However, this proved unsuccessful, most likely because in the cross-linked material, the local concentration of the reactants is always relatively high.



Scheme 4: Synthesis and polymerization of monomer **13d**.

During the preparation of monomer **13c** we were concerned that the cinnamyl side chain might undergo unwanted metathesis reactions, causing end-capping and broadened molecular weight distributions. Therefore, for comparison,

monomer **13d** was prepared by hydrogenation of amine **10c**, followed by reaction with maleic anhydride and esterification (Scheme 4). In the event, monomer **13c** did not undergo unwanted metathesis reactions and gave polymers with narrow polydispersity which did not increase with time (Table 5) and gave a linear correlation between **13c:14** ratio and molecular weight (Figure 6 and Table 6).

Table 5. Homopolymerization of monomer **13c**.^[a]

Time (min)	M _n (Da)	M _w (Da)	Đ
10	4160	45562	1.10
15	42592	47260	1.11
20	44745	50249	1.12
30	47076	53237	1.13
40	47190	55231	1.17
50	46874	54125	1.15

[a] All reactions were carried out at 25 °C in dichloroethane using a monomer to catalyst ratio of 100:1 and a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent). Conversion of monomer could not be precisely determined by NMR due to an overlap of monomer and polymer signals but was complete at 50 minutes.

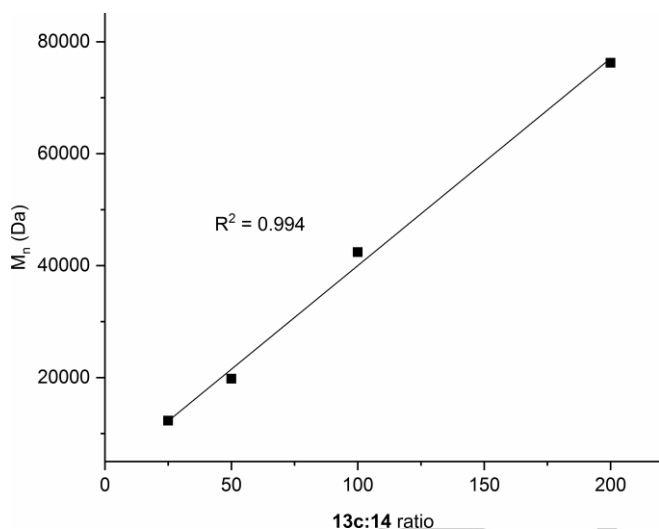


Figure 6: Linear relationship of molecular weight (M_n determined by SEC) to the **13c:14** ratio.

Table 6. Molecular weight data for the homopolymerization of monomer **13c** at various ratios to catalyst **14**.^[a]

13c:14 ratio	M _n (Da)	M _w (Da)	Đ
25:1	12298	13131	1.07
50:1	19783	21123	1.07
100:1	42410	46836	1.1
200:1	76240	83900	1.1

[a] All reactions were carried out at 25 °C in dichloroethane for 60 minutes using a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent). All reactions had gone to completion after 60 minutes.

Homopolymerization of monomer **13d** also did not show evidence of increased polydispersity with increased reaction time (Table 7), though the observed polydispersities were slightly higher than those observed for the other comparable homopolymers. A linear relationship was again observed between the **13d:14** ratio and the polymer molecular weight (Figure 7 and Table 8).

Table 7. Homopolymerization of monomer **13d** at a 100:1 **13d:14** ratio.^[a]

Time (min)	Conversion %	M _n (Da)	M _w (Da)	Đ
10	54	40410	44879	1.11
20	73	49178	55255	1.12
40	91	54228	64160	1.18
60	91	57946	66938	1.16

[a] All reactions carried out in dichloroethane at room temperature with a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent).

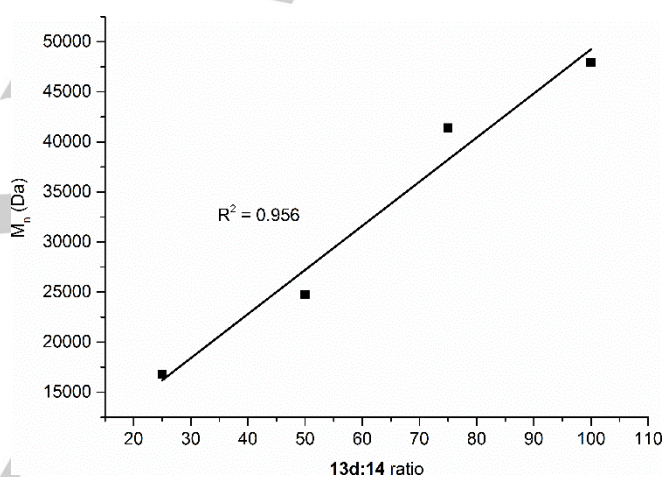


Figure 7: Linear relationship of molecular weight (M_n determined by SEC) to the **13d:14** ratio.

Table 8: Molecular weight data for the homopolymerization of monomer **13d** at various ratios to catalyst **14**.^[a]

13d:14 ratio	M _n (Da)	M _w (Da)	Đ
25:1	16773	17989	1.07
50:1	24749	28018	1.13
75:1	41398	47379	1.14
100:1	47946	66938	1.15

[a] All reactions were carried out at room temperature in dichloroethane for 60 minutes using a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent). All reactions had gone to completion in 60 minutes.

Having established that homopolymerizations were well-controlled, copolymerizations were investigated. Copolymerization of an equimolar ratio of benzyl and furfuryl monomers in a 50:50:1 **13a:13b:14** ratio was carried out with both monomers added at the start of the reaction. As both monomers were known to polymerize at essentially the same

rate (Figure 4), this was expected to produce a random copolymer. The reaction was monitored over time to ensure complete conversion (Table 9). The polymerization was complete after 30 minutes and polymer with a narrow molecular weight distribution was formed throughout the reaction.

Table 9. Random copolymerization of 50:50:1 **15a:15b:16**.^[a]

Time (min)	M _n (Da)	M _w (Da)	Đ	Conversion (%)
5	36748	38363	1.04	88
10	41499	44231	1.07	96
20	42813	46600	1.08	98
30	44125	47239	1.07	100

[a] Reactions carried out in dichloroethane at room temperature using a catalyst concentration of 0.57 mM (2 mg **14** in 4 ml solvent).

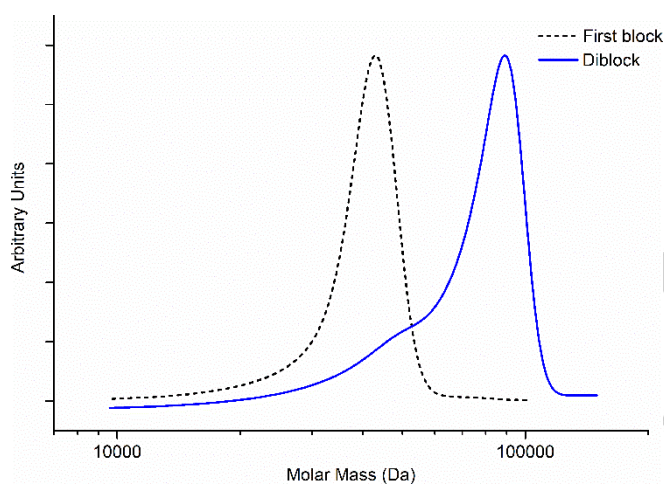


Figure 8: SEC of 100:1 homopolymer of **13a** (the first block of the copolymer), and 100:50:1 diblock copolymer of **13a** and **13b**.

A block copolymer was then prepared by first polymerizing a block of monomer **13a** (100:1 monomer:catalyst **14**). After 10 minutes, monomer **13a** was 96% consumed, so 50 equivalents of monomer **13b** were added and the polymerization allowed to continue for a further 30 minutes (Table 10). Figure 8 shows the SEC traces obtained on the intermediate homopolymer of **13a** and the final block copolymer. A minor shoulder is apparent in the SEC trace of the block copolymer, corresponding to some dead ends of the homopolymer of monomer **13a**. If the polymerization of monomer **13a** was left for longer than 10 minutes, then the shoulder became more pronounced and the dispersity of the block copolymer increased.

Table 10. Diblock copolymerization of monomer **13a** and **13b**.

Ratio 15a:15b:16	Time (min)	M _n (Da)	M _w (Da)	Đ	Conversion (%)
100:0:1	10	37105	39938	1.08	96
100:50:1	40	61769	74825	1.21	98

Thermal analysis of this family of homo- and copolymers revealed that they all have remarkable thermal stability, with decomposition (T_{10%}) starting between 340 and 383 °C. These values are comparable to those we have previously reported for polymers obtained from esters and amides of acid **8**.^[11,13,19] Differential scanning calorimetry in the range -60 to 250 °C using "pinhole" sample pans indicated that the homo- and co-polymers of **13a**, **13b** and **13c** all had glass transitions (T_g) in the range 160-168 °C. The homopolymer of **13d** did not give good DSC results under these conditions, but could be analysed using a sealed pan with a temperature range of -60 to 280 °C and showed a T_g of 101 °C. This lower T_g is probably due to the more flexible nature of the pendant phenylpropyl substituent, and is consistent with the lower melting point of the corresponding monomer **13d**.

Table 11. Screening of alternative solvents for the polymerization of **13a** at a 100:1 ratio with catalyst **14**.

Solvent	13a Solubility	Time (min)	Conversion (%)	M _n	M _w	Đ
DCE	Yes	30	100	57010	60568	1.07
		10	91.2			
THF	Yes	20	98.8			
		30	100	51196	54593	1.07
DMC	Yes	10	83.8			
		20	95.8			
MEK	Yes	30	98.5	46022	49471	1.07
		10	15.3	-	-	-
		20 hours	23.7	-	-	-
2-MeTHF	Poor	-	-	-	-	-
EtOAc	Poor	-	-	-	-	-
DEC	Poor	-	-	-	-	-
tBuOAc	Poor	-	-	-	-	-
TMO	No	-	-	-	-	-

Monomers derived from acid **8** would only undergo ROMP at useful rates in chlorinated solvents which severely compromised the greenness of the polymerization process. However, as monomers **13** polymerize several orders of magnitude faster than monomers derived from **8**, a variety of alternative solvents were screened as potential replacements for dichloroethane. Tetrahydrofuran (THF), dimethyl carbonate^[21] (DMC), methyl ethyl ketone (MEK), 2-methyl tetrahydrofuran^[22] (2-MeTHF), ethyl acetate (EtOAc), diethyl carbonate (DEC), and 2,2,5,5-tetramethyloxolane^[23] (TMO) were initially screened for their ability to dissolve monomer **13a**. Of these, only THF, DMC, and MEK dissolved the monomer quickly. ROMP of monomer **13a** was then successful in both THF and DMC, with the reaction reaching completion within 30 minutes and giving polymer with a similar molecular weight to that produced in dichloroethane (Table 11). Only very slow polymerization was observed in MEK, possibly due to coordination of the ketone to the catalyst. Dimethyl carbonate can be produced either (indirectly) from carbon dioxide via the transesterification of cyclic carbonates with methanol, or directly from carbon

monoxide, methanol and oxygen and is known to have very low toxicity.^[24] Whilst THF is less hazardous than dichloroethane, it is still considered to be “problematic” in terms of toxicity,^[25] so for most purposes DMC would be preferred. The rate of initiation of **14** may differ between these solvents,^[26] however the low polydispersity of the resulting polymers showed that initiation was still very fast^[20] compared to propagation.

Conclusions

Monomers **13a-d** constitute a new class of monomers for ring opening metathesis polymerization (ROMP) which are prepared from biomass derived precursors by a highly atom-economical route. These monomers demonstrate well-controlled ROMP with Grubbs 3rd generation catalyst, giving polymers with narrow molecular weight distributions and a linear relationship between molecular weight and the monomer-catalyst ratio. Random and block copolymers were prepared from the benzyl and furfuryl monomers (**13a** and **13b**). The copolymers also had narrow polydispersity consistent with a “living” polymerization, which is confirmed by the observed increase in molecular weight for the diblock copolymerization without a significant increase in polydispersity. In all cases, these monomers polymerize orders of magnitude faster than those developed in our previous work,^[11,13,19] with polymerizations typically being completed in a matter of minutes. This rapid rate of polymerization allowed the polymerizations to be carried out in non-halogenated solvents such as THF and dimethyl carbonate, the latter being preferred due to its low toxicity and more sustainable production. The furfuryl monomer **13b** was interesting in demonstrating self-crosslinking at higher monomer:catalyst ratios, believed to be as a result of a Diels-Alder reaction between the pendant furan moiety and the alkenes of the polymer backbone.

Experimental Section

Maleic anhydride, furfurylamine, sodium borohydride and aldehydes were purchased from Sigma Aldrich and were used as received. Ethanol and methanol were kept over activated molecular sieves for a minimum of 24 hours before use. Grubbs 3rd Generation Catalyst was purchased from Sigma Aldrich and stored at 4 °C.

NMR spectroscopy was carried out on a Jeol 400MHz instrument in the indicated solvent, and spectra are referenced to the residual solvent signal. Fully assigned ¹H and ¹³C spectra of oxa-norbornenes **12** and **13** are given in the supporting information. Infrared spectra were obtained using a Perkin Elmer Spectrum 400 FT-IR instrument. High resolution mass spectra were recorded using Electrospray Ionization (ESI), on a Bruker micrOTOF mass spectrometer in tandem with an Agilent series 1200 Liquid Chromatography (LC) system. Melting points were determined using either a Stuart SMP3 or SMP20 hot stage apparatus and were not corrected.

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Cu-K_α radiation ($\lambda = 1.54184 \text{ \AA}$) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell

determination, frame integration and unit-cell refinement was carried out with “Crisalis”.^[27] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.^[28] OLEX2^[29] was used for overall structure solution, refinement and preparation of publication data. Within OLEX2, the algorithms used for structure solution were “ShelXT dual-space”^[30] Refinement by full-matrix least-squares used the SHELXL-97^[31] algorithm within OLEX2.^[29] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions.

SEC was carried out using a set (PSS SDV High) of 3 analytical columns (300 x 8mm, particle diameter 5 μm) of 1000, 10⁵ and 10⁶ \AA pore sizes, plus a guard column, supplied by Polymer Standards Service GmbH (PSS) installed in a PSS SECcurity SEC system. Elution was with THF at 1 ml/min with a column temperature of 23 °C and detection by refractive index. 20 μL of a 1 mg/ml sample in THF, with a small quantity of toluene added as a flow marker, was injected for each measurement and eluted for 50 minutes. Calibration was carried out in the molecular weight range 400–2x10⁶ Da using ReadyCal polystyrene standards supplied by Sigma Aldrich, and referenced to the toluene peak.

Thermogravimetric analysis (TGA) was carried out using a PL Thermal Sciences STA 625 instrument from ambient (22 °C) to 600 °C at a ramp rate of 10 degrees per minute in an open aluminium sample pan under N₂. Differential scanning calorimetry (DSC) was carried out using a TA Instruments MDSC Q2000 instrument in either closed or “pinhole” aluminium sample pans under N₂.

Synthesis of secondary amines 10a–c. Furfurylamine **3** (9.7 g, 0.1 mol) and an aldehyde **11a–c** (0.1 mol) were dissolved in ethanol (185 mL). The mixture was stirred under a nitrogen atmosphere for 1 hour, after which time sodium borohydride (7.6 g, 0.2 mol) was added and the mixture stirred for a further 16 hours. The reaction was then diluted with deionized water (200 mL), adjusted to pH 1 with 1M hydrochloric acid, and washed with CH₂Cl₂ (3x150 mL). The aqueous phase was then adjusted to pH 10 with 1M aqueous sodium hydroxide, after which the product was extracted with CH₂Cl₂ (3x100 mL) and washed with brine (3x100 mL). The organic phase was dried (MgSO₄) and solvent removed *in vacuo* to give secondary amines **10a–c**.

N-Benzyl(furan-2-ylmethyl)amine 10a.^[32] Obtained as a yellow oil (72%); ¹H NMR (400 MHz, CDCl₃): δ 7.39 (1H, dd *J* 0.8, 1.8 Hz, Furan-*H*), 7.4–7.3 (4H, m, Ar-*H*), 7.3–7.1 (1H, m, Ar-*H*), 6.33 (1H, dd *J* 1.9, 3.1 Hz, Furan-*H*), 6.19 (1H, dd *J* 0.8, 3.2 Hz, Furan-*H*), 3.79 (4H, s, CH₂NHCH₂), 1.68 (1H, s, NH). ¹³C NMR (100.5 MHz, CDCl₃): δ 153.9, 141.9, 139.9, 128.5, 128.3, 127.1, 110.2, 107.1, 52.8, 45.4; IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3027, 2831, 1602; HRMS (ESI) *m/z*: Calcd for C₁₂H₁₄NO (MH⁺) 188.1070, found 188.1071.

Bis((furan-2-yl)methyl)amine 10b.^[33] Obtained as a white solid (84%); ¹H NMR (400 MHz, CDCl₃): δ 7.36 (2H, dd *J* 0.8, 1.7 Hz, Furan-*H*), 6.31 (2H, dd *J* 1.9, 2.9 Hz, Furan-*H*), 6.19 (2H, d *J* 3.2 Hz, Furan-*H*), 3.78 (4H, s, (CH₂)N), 1.82 (1H, s, NH). ¹³C NMR (100.5 MHz, CDCl₃): δ 153.5, 142.1, 110.2, 107.4, 45.1. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3117, 2916, 2834, 1599, 1505, 1146. HRMS (ESI) *m/z*: Calcd for C₁₀H₁₂NO₂ (M+Na)⁺ 178.0863, found 178.0861.

N-Cinnamyl(furan-2-ylmethyl)amine 10c. Further purified by chromatography on silica eluting with 3:2 EtOAc:petroleum ether (R_f = 0.3). Obtained as a yellow oil (41%). ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.1 (6H, m, Furan-*H* and 5 Ar-*H*), 6.54 (1H, d *J* 15.9 Hz, =CHPh), 6.30 (2H, m, Furan-*H* and CH=CHPh), 6.20 (1H, dd, *J* 0.6, 3.1 Hz, Furan-*H*),

3.83 (2H, s, Furan-CH₂), 3.42 (2H, dd *J* 1.4, 6.4 Hz, CH₂-CH=CH), 1.67 (1H, s, NH). ¹³C NMR (100.5 MHz, CDCl₃): δ 153.8, 142.0, 137.2, 131.9, 128.7, 128.1, 127.5, 126.4, 110.3, 107.2, 51.0, 45.5. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3025, 2917, 1667, 1494, 1448, 1146. HRMS (ESI) *m/z*: Calcd for C₁₄H₁₆NO (M+Na)⁺ 214.1226, found 214.1230.

N-3-Phenylpropyl(furan-2-ylmethyl)amine 10d.^[34] Cinnamyl derivative **10c** (1.0 g, 4.7 mmol) was dissolved in methanol (10 mL) and 10% palladium on carbon (50 mg) was added. The mixture was thoroughly degassed with argon, then hydrogen was bubbled through the reaction mixture for 10 minutes. The mixture was left stirring under hydrogen for 24 hours before being thoroughly purged with argon. The reaction mixture was diluted with EtOAc (50 mL), filtered through silica and the solvent removed *in vacuo* to give compound **10d** as a yellow oil (95%). ¹H NMR (400 MHz, CDCl₃): δ 7.36 (1H, dd *J* 0.7, 1.8 Hz, Furan-H), 7.3–7.2 (2H, m, Ar-H), 7.2–7.1 (3H, m, Ar-H), 6.31 (1H, dd *J* 1.9, 3.1 Hz, Furan-H), 6.16 (1H, d *J* 3.2 Hz, Furan-H), 3.78 (2H, s, Furan-CH₂), 2.66 (4H, m, NHCH₂CH₂CH₂Ph), 1.83 (2H, dt *J* 7.5, 9.3 Hz, CH₂CH₂Ph), 1.55 (1H, s, NH). ¹³C NMR (100.5 MHz, CDCl₃): δ 154.1, 142.2, 141.9, 128.5, 128.4, 125.9, 110.2, 106.9, 48.7, 46.3, 33.7, 31.7. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3025, 2925, 1602, 1495, 1453, 1146. HRMS (ESI) *m/z*: Calcd for C₁₄H₁₈NO (M+Na)⁺ 216.1383, found 216.1385.

Synthesis of oxa-norbornene lactams 12a-d. Secondary amine **10a-d** (81.0 mmol) and maleic anhydride **7** (7.9 g, 81.0 mmol) were stirred together in toluene (100 mL) for 16 hours. The reaction was concentrated *in vacuo* and the resulting solid recrystallized from acetone to give the products as white crystalline solids.

3-Benzyl-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic acid 12a.^[35] Obtained as colourless crystals (55%). Mp 171.5–172.3 °C (lit.^[35] 170–174 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.2 (5H, m), 6.44 (1H, dd *J* 1.6, 5.8 Hz), 6.41 (1H, d *J* 5.8 Hz), 5.30 (1H, d *J* 1.6 Hz), 4.66 (1H, d *J* 14.9 Hz), 4.43 (1H, d *J* 14.9 Hz), 3.85 (1H, d *J* 12.0 Hz), 3.67 (1H, d *J* 12.0 Hz), 2.94 (1H, d *J* 9.1 Hz), 2.86 (1H, d *J* 9.1 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 173.2, 172.7, 137.4, 135.3, 134.9, 129.1, 128.1, 128.1, 89.0, 82.5, 50.8, 48.7, 47.2, 46.1. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3013, 2919, 1736, 1651, 1202, 1174. HRMS (ESI) *m/z*: Calcd for C₁₆H₁₆NO₄ (MH)⁺ 286.1074, found 286.1072.

3-(Furan-2-ylmethyl)-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic acid 12b.^[36] Obtained as colourless crystals (95%). Mp 150.9–151.7 °C (lit.^[36] 150–151 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.37 (1H, dd *J* 0.7, 1.7 Hz), 6.46 (2H, d *J* 0.6 Hz), 6.33 (1H, dd *J* 1.9, 3.2 Hz), 6.30 (1H, d *J* 3.2 Hz), 5.29 (1H, s), 4.79 (1H, d *J* 15.6 Hz), 4.27 (1H, d *J* 15.6 Hz), 3.94 (1H, d *J* 12.0 Hz), 3.78 (1H, d *J* 12.0 Hz), 2.91 (1H, d *J* 9.1 Hz), 2.84 (1H, d *J* 9.1 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 173.6, 172.1, 149.2, 142.8, 137.3, 135.1, 110.7, 109.0, 88.9, 82.4, 50.8, 49.1, 45.7, 40.0. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3141, 2956, 1726, 1693, 1172. HRMS (ESI) *m/z*: Calcd for C₁₄H₁₃NNaO₅ (M+Na)⁺ 298.0686, found 298.0683.

3-Cinnamyl-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic acid 12c. Obtained as a white solid (73%). Mp 158.6–158.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.2 (5H, m), 6.59 (1H, d *J* 16.0 Hz), 6.49 (1H, dd *J* 5.6, 1.6 Hz), 6.44 (1H, d *J* 5.6 Hz), 6.10 (1H, dt *J* 16.0, 6.4 Hz), 5.36 (1H, d *J* 1.6 Hz), 4.22 (1H, dd *J* 15.2, 5.6 Hz), 4.06 (1H, dd *J* 15.2, 5.6 Hz), 4.01 (1H, d *J* 12.0 Hz), 3.80 (1H, d *J* 12.0 Hz), 2.92 (1H, d *J* 9.2 Hz), 2.88 (1H, d *J* 9.2 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 172.9, 172.6, 137.5, 136.2, 134.9, 134.2, 128.8, 128.2, 126.7, 122.4, 89.1, 82.6, 50.7, 48.9, 46.2, 45.4. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 2913, 1699, 1638. HRMS (ESI) *m/z*: Calcd. for C₁₈H₁₇NNaO₄ (M+Na)⁺ 334.1050, found 334.1043.

3-(3-Phenylpropyl)-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylic acid 12d. Obtained as white crystals (72%). Mp 131.2–132.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.3–7.1 (5H, m), 6.42 (1H, dd *J* 1.6, 5.8 Hz), 6.39 (1H, d *J* 5.8 Hz), 5.25 (1H, d *J* 1.5 Hz), 3.91 (1H, d *J* 11.9 Hz), 3.71 (1H, d *J* 11.9 Hz), 3.48 (1H, dd *J* 7.1, 14.1 Hz), 3.29 (1H, dd *J* 7.0, 13.9 Hz), 2.84 (1H, d *J* 9.2 Hz), 2.81 (1H, d *J* 9.1 Hz), 2.7–2.5 (2H, m), 1.9–1.7 (2H, m). ¹³C NMR (100.5 MHz, CDCl₃): δ 173.2, 172.8, 141.3, 137.4, 134.9, 128.6, 128.5, 126.1, 89.0, 82.5, 50.8, 49.1, 46.0, 43.0, 33.0, 28.6. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3018, 2936, 1727, 1663, 1180. HRMS (ESI) *m/z*: Calcd for C₁₈H₁₉NNaO₄ (M+Na)⁺ 336.1206, found 336.1204.

Synthesis of methyl esters 13a–d. Carboxylic acid **12a–d** (6.7 mmol) was dissolved in methanol (20 mL), one drop of sulfuric acid was added and the reaction was heated at reflux for 16 hours. The reaction mixture was diluted with deionized water (10 mL) and adjusted to pH 8 with 1M aqueous NaHCO₃, after which the methanol was removed *in vacuo*. In the case of ester **13a**, the product precipitated as white crystals. In all other cases, the product was extracted with CH₂Cl₂ (3x15 mL), which was then washed with brine (20 mL), dried (MgSO₄) and concentrated *in vacuo* to give esters **13b–d**.

Methyl 3-benzyl-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylate 13a.^[37] Obtained as colourless crystals (95%). Mp 110.5–111.9 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.2 (5H, m), 6.47 (1H, d *J* 5.6 Hz), 6.43 (1H, dd *J* 1.6, 5.9 Hz), 5.17 (1H, d *J* 1.7 Hz), 4.67 (1H, d *J* 15.0 Hz), 4.34 (1H, d *J* 15.0 Hz), 3.9–3.8 (4H, m), 2.83 (1H, d *J* 9.1 Hz), 2.76 (1H, d *J* 9.1 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 172.4, 170.8, 137.0, 136.0, 135.4, 128.9, 128.0, 127.7, 88.6, 81.5, 52.3, 51.2, 48.2, 46.8, 44.9. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3002, 2949, 1727, 1686, 1175. HRMS (ESI) *m/z*: Calcd for C₁₇H₁₇NNaO₄ (M+Na)⁺ 322.1050, found 322.1058.

Methyl 3-(Furan-2-ylmethyl)-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylate 13b. Obtained as colourless crystals (77%). Mp 104.3–105.2 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.35 (1H, dd *J* 0.7, 1.8 Hz), 6.48 (1H, d *J* 5.9 Hz), 6.43 (1H, dd *J* 1.7, 5.9 Hz), 6.32 (1H, dd *J* 1.8, 3.2 Hz), 6.27 (1H, dd *J* 0.7, 3.2 Hz), 5.16 (1H, d *J* 1.6 Hz), 4.78 (1H, d *J* 15.6 Hz), 4.19 (1H, d *J* 15.6 Hz), 3.92 (1H, d *J* 11.8 Hz), 3.8–3.7 (4H, m), 2.80 (1H, d *J* 9.1 Hz), 2.73 (1H, d *J* 9.1 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 172.4, 170.5, 149.9, 142.6, 137.1, 135.4, 110.7, 108.5, 88.6, 81.5, 52.4, 51.1, 48.8, 44.9, 39.8. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 2951, 1732, 1684, 1505. HRMS (ESI) *m/z*: Calcd for C₁₅H₁₅NNaO₅ (M+Na)⁺ 312.0842, found 312.0842.

Methyl 3-cinnamyl-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylate 13c. Obtained as colourless crystals (89%). Mp 122.1–122.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.4–7.2 (5H, m), 6.57 (1H, d *J* 16.0 Hz), 6.51 (1H, d *J* 6.0 Hz), 6.45 (1H, dd *J* 6.0, 2.0 Hz), 6.11 (1H, dt *J* 16.0, 6.4 Hz), 5.19 (1H, d *J* 1.6 Hz), 4.22 (1H, dd *J* 15.2, 10.0 Hz), 3.99 (1H, dd *J* 15.2, 10.0 Hz), 3.98 (1H, d *J* 12.0 Hz), 3.79 (3H, s), 3.77 (1H, d *J* 13.2 Hz), 2.84 (1H, d *J* 9.0 Hz), 2.76 (1H, d *J* 9.0 Hz). ¹³C NMR (100.5 MHz, CDCl₃): δ 172.4, 170.5, 137.0, 136.4, 135.5, 133.5, 128.7, 127.9, 126.6, 123.2, 88.7, 81.5, 52.3, 51.3, 48.4, 45.0, 44.9. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 3022, 2950, 2905, 1734, 1694, 1596, 1575. HRMS (ESI) *m/z*: Calcd. for C₁₉H₁₉NNaO₄ (M+Na)⁺ 348.1206, found 348.1194.

Methyl 3-(3-Phenylpropyl)-4-oxo-10-oxa-3-azatricyclo[5.2.1.0^{1,5}]dec-8-ene-6-carboxylate 13d. Purified by column chromatography on silica eluting with EtOAc and obtained as a waxy white solid (100%). Mp 84–87 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.3–7.2 (2H, m), 7.2–7.1 (3H, m), 6.48 (1H, d *J* 5.8 Hz), 6.43 (2H, dd *J* 5.8, 1.7 Hz), 5.16 (1H, d, *J* 1.7 Hz), 3.88 (1H, d *J* 11.6 Hz), 3.77 (3H, s), 3.69 (1H, d *J* 11.6 Hz), 3.6–3.4 (1H, m), 3.4–3.2 (1H, m), 2.8–2.5 (4H, m), 1.9–1.8 (2H, m). ¹³C NMR (101

MHz,) δ = 172.4, 170.7, 141.6, 137.0, 135.5, 128.5, 128.5, 126.0, 88.6, 81.5, 52.3, 51.3, 48.6, 44.9, 42.7, 33.1, 28.9. IR (neat, ATR) $\nu_{\text{max}}/\text{cm}^{-1}$ 2918, 1721, 1674. HRMS (ESI) m/z : Calcd. For $\text{C}_{19}\text{H}_{21}\text{NNaO}_4$ (M+Na)⁺ 350.1363, found 350.1356.

General method for polymerizations. Grubbs 3rd generation catalyst **14** (2.0 mg, 0.57 mmol) and the appropriate quantity of solid monomer **13a-d** were added to a glass vial containing a magnetic stirrer bar and thoroughly degassed by three cycles of evacuation and filling with argon. 1,2-Dichloroethane (or an alternative solvent) was separately degassed by freezing with liquid nitrogen and thawing under vacuum three times before back-filling with argon. This solvent (4 mL) was then used to dissolve the monomer and catalyst. The reaction was stirred for the appropriate duration at 25 °C, before end-capping by the addition of excess ethyl vinyl ether (1 drop, stirred for 10 minutes). An aliquot of the reaction mixture was concentrated and dissolved in CDCl_3 for analysis by NMR spectroscopy to determine the degree of conversion. The remaining solution was passed through a short (2 cm) silica pad to remove residual catalyst and the silica was flushed with CH_2Cl_2 . The volume of solvent was reduced *in vacuo* if necessary and the polymer precipitated into cold hexane which was refrigerated until the polymer was settled. The hexane was carefully decanted and the polymer dried *in vacuo* prior to further analysis.

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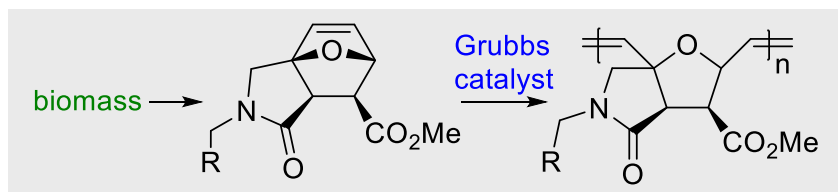
Keywords: Ring-Opening Metathesis Polymerisation • biomass • bio-based • living polymerisation • sustainable polymer

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Layout 2:

FULL PAPER



Monomers obtained from sustainably sourced furfuryl amines and maleic anhydride undergo rapid and controlled ROMP when treated with Grubbs third generation catalyst.

Anna Blanpain, James H. Clark, Thomas J. Farmer, Yuanlong Guo, Ian D. V. Ingram, John E. Kendrick, Stefan B. Lawrenson, Michael North, George Rodgers and Adrian Whitwood*

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Rapid ring-opening metathesis polymerization of monomers obtained from biomass derived furfuryl amines and maleic anhydride