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1. Green Chemistry Centre of Excellence, Department Of Chemistry, University of York, York, UK, YO10 5DD. Email: thomas.farmer@york.ac.uk, james.clark@york.ac.uk, michael.north@york.ac.uk.

† Current address: Department of Chemistry, Northwest University, Xi’an, Shaanxi, China

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Wholly biomass derivable sustainable polymers by ring-opening metathesis polymerisation of monomers obtained from furfuryl alcohol and itaconic anhydride

Yinjuan Bai,a† James H. Clark,a Thomas J. Farmer,a Ian D. V. Ingram,a and Michael North\*a

Ring-opening metathesis polymerisation (ROMP) of oxanorbornene esters by Grubbs second generation catalyst is used to prepare a range of wholly biomass-derivable homo and copolymers. Eight ester monomers are prepared by esterification of the corresponding carboxylic acid which itself is formed by a 100% atom-economical tandem Diels-Alder-lactonisation reaction of itaconic anhydride and furfuryl alcohol. The well-controlled nature of the ROMP is confirmed by NMR studies and facilitated the preparation of homopolymers, random copolymers and block copolymers with good control over the polymer molecular weight and molecular weight distribution.

Introduction

Synthetic polymers are produced on a scale of more than 300 million metric tonnes annually[[1]](#endnote-2) and the vast majority are produced from petrochemical sources. This accounts for around 4% of crude oil consumption, the largest sector after fuels (87%).[[2]](#endnote-3) The demand for plastics along with their ubiquity in technology, packaging, and consumer products, means that the polymer industry will have to be a key part of a future bio-based economy. In order to be of genuine interest, any feedstock for polymer production ought to be available at reasonable cost from biomass on a scale commensurate with the production of polymers. Even for niche applications, this implies the availability of tonnes rather than grams of material. To address this issue, it is already envisaged that monomers derived from highly abundant lignocellulose will be vital to a sustainable polymer industry.[[3]](#endnote-4)

Itaconic acid **1** (Figure 1)has been produced at scale by fermentation for decades.[[4]](#endnote-5) Newer organisms are allowing a greater use of cellulosic waste, so-called ‘second generation’ biomass, for production of itaconic acid.[[5]](#endnote-6),[[6]](#endnote-7) It is predicted that annual production of itaconic acid will reach 400,000 tonnes by 2020.[[7]](#endnote-8) Furan derivatives are producible from a variety of sugars and cellulosic biomass with chloromethyl furfural (CMF, **2**) and hydroxymethyl furfural (HMF, **3**) being of particular current interest.[[8]](#endnote-9),[[9]](#endnote-10),[[10]](#endnote-11) Furfural **4** is also already produced in large quantities (hundreds of thousands of tonnes per year)



**Figure 1:** Bio-based platform molecules **1–4** and derived starting materials **5** and **6**.

from agricultural waste,[[11]](#endnote-12) Furan derivatives **2–4**, alongside itaconic acid **1**, are already widely anticipated to be key platform molecules for the bio-based chemicals industry of the future.[[12]](#endnote-13),[[13]](#endnote-14)

Poly(alkyl)itaconates, and their copolymers, derived from esters of itaconic acid,[[14]](#endnote-15),[[15]](#endnote-16) and prepared by conventional radical polymerisations,[[16]](#endnote-17),[[17]](#endnote-18),[[18]](#endnote-19),[[19]](#endnote-20) are well established in the literature as are polyesters derived from itaconic acid and a diol.[[20]](#endnote-21) However, simple poly(alkyl)itaconates invariably have a glass transition temperature (Tg) well below room temperature, resulting in gum-like materials. This restricts the uses of these polymers and excludes them from applications in engineering materials or packaging as substitutes for the ubiquitous and versatile polyacrylates and similar materials for which they might at first appear to be useful biobased replacements. Poly(benzyl)itaconates, by contrast, are reported to be glassy solids at room temperature,[[21]](#endnote-22) however, these are less readily produced in a sustainable way due to the difficulty in sourcing simple benzene derivatives from biomass.[[22]](#endnote-23) Therefore, we initiated a project aimed at producing a bio-based analogue of benzyl itaconates by esterification of itaconic acid **1** or the derived cyclic anhydride **6,** which may be produced directly by reactive distillation of citric acid,[[23]](#endnote-24) (which is itself a product of fermentation[[24]](#endnote-25)) with furfuryl alcohol **5** obtainable by reduction of furfural **4**.[[25]](#endnote-26)



**Scheme 1:** Previously reported synthesis and ROMP of monomer **8a**

However, as we recently reported,[[26]](#endnote-27) reaction of anhydride **6** with alcohol **5** led not to an itaconate ester, but rather gave oxa-norbornene derivative **7** as the only product (Scheme 1). This observation was also reported independently and simultaneously by Hoye *et al*. who were investigating the Diels-Alder addition of itaconic anhydride **6** to a range of furans.[[27]](#endnote-28) Compound **7** is formed as a result of a tandem Diels-Alder cycloaddition and lactone formation, with the product crystallising from solution, or from the neat reaction mixture. It is believed that the Diels-Alder addition occurs rapidly and reversibly, as is typical of Diels-Alder additions to furans,[[28]](#endnote-29),[[29]](#endnote-30),[[30]](#endnote-31) and that the second step is lactone formation, with the overall reaction being driven by the crystallisation of polycyclic oxa-norbornene carboxylic acid **7**. This tandem reaction is 100% atom economical, is performed at room temperature in air and does not require solvents, catalysts or other auxiliaries. As a fully bio-derived molecule made in a virtually waste-free process (except for a small amount of solvent used for washing or recrystallisation), acid **7** is a very promising candidate for green and sustainable polymer chemistry.

We previously reported24 that the methyl ester **8a** of acid **7** could be polymerised to homopolymer **9a** by Ring Opening Metathesis Polymerisation (ROMP)[[31]](#endnote-32) on treatment with second generation Grubbs catalyst **10**.[[32]](#endnote-33) This was the first report of ROMP of a substrate with the hindered substitution pattern around the oxa-norbornene bridgehead present in monomer **8a**. The methyl ester in **8a** is also on the *endo*-face of the norbornene ring and *endo*-substituents are known to retard the rate of ROMP reactions.[[33]](#endnote-34) Homopolymer **9a** was unfortunately found to have very poor solubility in a range of solvents which hampered its characterisation. Therefore, we prepared random copolymers **11** from methyl ester **8a** and commercial norbornene **12**. These copolymerisations gave polymers which were soluble in organic solvents such as chloroform and THF and were shown to be living polymerisations as a linear relationship between the monomer:catalyst ratio and the molecular weight was determined by SEC.

In the present study, we show that the previous method developed for the synthesis and ROMP of monomer **8a** can be extended to a range of esters **8a-h** including those derived from bio-based alcohols, giving wholly bio-based monomers which undergo ROMP to give homo- and co-polymers. Provided the alcohol contains at least five carbon atoms, the resulting polymer is soluble in organic solvents such as dichloromethane and THF.

Experimental

Materials.

Carboxylic acid **7** was prepared as described previously.24 Anhydrous CH2Cl2 was obtained from a solvent purification system by passage through a dry alumina column. All other reagents were purchased from Sigma Aldrich and used without purification.

General synthesis of 1-oxo-6,7-dihydro-3a,6-epoxy-2-benzofuran-7a(1H,3H)-yl) alkyl esters 8a-h.

1-oxo-6,7-dihydro-3a,6-epoxy-2-benzofuran-7a(1H,3H)-yl) acetic acid **7** (1.05 g, 5.0 mmol) was suspended in anhydrous CH2Cl2 (5 ml) under argon at 0 °C. To this suspension was added a 2.0 M solution of oxalyl chloride in CH2Cl2 (6 ml) and one drop of DMF. The resulting mixture was stirred and allowed to warm to room temperature for 2 hours, after which time a homogeneous solution had formed. The reaction mixture was concentrated to dryness under vacuum, taking care not to expose the material to air in order to minimise hydrolysis. The unpurified acyl chloride **14** was dissolved in anhydrous CH2Cl2 (5 ml) under argon. To this stirred solution was added a CH2Cl2 solution containing 3 equivalents of triethylamine (2.1 ml, 1.5 g) and 0.9 equivalents (4.5 mmol) of alcohol **13a–h**. The reaction was stirred at room temperature for 16 h under argon before being washed sequentially with 1M aq. HCl (10 ml), 1 M aq. NaHCO3 (10 ml), water (10 ml), and brine (10 ml), dried (MgSO4), and concentrated *in vacuo*. The residue was purified by flash chromatography on silica, eluting with n-hexane and EtOAc to give esters **8a-h**. Characterising data for each monomer is given in the supporting information.

General procedure for ROMP polymerisation.

The appropriate quantities of monomer(s) **8a-h** and Grubbs 2nd generation catalyst **10** were separately dissolved in (CH2Cl)2. Each solution was subjected to degassing by three freeze-thaw cycles under vacuum and back-filled with argon. The solution of the catalyst was then added to that containing the monomer(s) and stirred for the appropriate time (in most cases, 72 h) under argon. After the allotted time, the polymerisation was terminated by addition of an excess of ethyl vinyl ether as a solution in CH2Cl2 followed by stirring for a further 30 minutes. The resulting solution was passed through a short column of silica gel to remove catalyst residues. An aliquot was concentrated *in vacuo* to confirm by 1H NMR spectroscopy that all of the monomer had been consumed. The remaining solution was precipitated into MeOH. After settling for several hours, the MeOH was carefully decanted and the solid polymer dried under reduced pressure.

Size Exclusion Chromatography (SEC).

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 Å pore sizes, plus 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 MePh 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.

Thermal Analysis.

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 a closed aluminium sample pan under N2 in a closed loop between -60 °C and 300 °C in all cases except homopolymer **9h**, where the maximum temperature was 165 °C.

Results and discussion

To overcome the insolubility associated with hompolymers **9a** of methyl ester **8a**, the synthesis of monomers with long-chain alkyl esters was investigated. To complement the 100% biomass derived nature of acid **7** the use of alcohols that could also be derived from biomass was a particular priority. Therefore, ester **8b** with a cetyl ester was the initial target as the linear C16 alcohol can be derived from a fatty acid.[[34]](#endnote-35) Unlike methyl ester **8a**, which can be made using conventional acid-catalysed esterification with methanol **13a**, the non-volatile nature of cetyl alcohol **13b** meant that it was more convenient to prepare this ester via acyl chloride **14**, which was synthesised using oxalyl chloride and a catalytic quantity of DMF (Scheme 2).

Cetyl ester **8b** was successfully polymerised under the same conditions used for methyl ester **8a**, using Grubbs second generation catalyst **10** in 1,2-dichloroethane at room temperature. The ratio between monomer **8b** and catalyst **10** was varied (Table 1) and the molecular weights of the resulting polymers **9b** determined by SEC (Figure 2). NMR analysis of these reactions showed no evidence for the formation of any product other than polymer **9b**. There was a linear relationship between monomer to catalyst ratio and number average molecular weight (Mn) (Figure 3), indicating that the polymerisation was a living process. This was supported by the narrow polydispersity indices of the polymers. However, whilst in our previous work on the copolymers **11** of methyl ester **8a** with norbornene **12** the molecular weights measured by SEC



**Scheme 2**: Preparation of monomers **8a-h** and homopolymers **9a-h** from acid **7**.

**Table 1:** Molecular weight data of homopolymers **9b** of cetyl ester **8b**.a

|  |  |  |  |
| --- | --- | --- | --- |
| **8b:10** | **Mn (SEC)** | **Mw (SEC)** | **Đ** |
| 25:1 | 13700 | 14728 | 1.08 |
| 50:1 | 18359 | 19044 | 1.04 |
| 75:1 | 23831 | 24642 | 1.03 |
| 100:1 | 27735 | 28825 | 1.04 |
| 200:1 | 42571 | 50096 | 1.17 |
| a) All reactions gave 100% conversion to polymer **9b** as determined by 1H NMR analysis of the polymerisation reactions. | | | |

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**Figure 2:** SEC of homopolymers **9b** of cetyl ester **8b** at various monomer:catalyst ratios.



**Figure 3:** Linear relationship between ratio of cetyl monomer **8b** to catalyst **10** and number average molecular weight measured by SEC for homopolymers **9b**.

agreed well with the calculated values, this was not the case with the cetyl homopolymers **9b**. This can be explained as the SEC is calibrated relative to polystyrene standards, and the volume occupied and solution morphology of comb-like polymer **9b**, with substantial alkyl pendant groups, is quite unlike polystyrene of the same molecular weight and therefore it elutes very differently on SEC. It is clear from Table 1 that at a 200:1 monomer:catalyst ratio, though the polymer molecular weight was close to the expected value, its polydispersity had begun to increase due to the increase in viscosity of the polymerisation solution. An attempt to avoid this problem by dilution of the 200:1 polymerisation resulted in the polymerisation becoming unacceptably slow, not reaching completion even after nine days.

Having established that soluble homopolymers of alkyl esters **8** could be formed, and that their polymerisation by ROMP was well defined, the size of alkyl group necessary to achieve a soluble polymer was investigated. Therefore, esters **8c–g** were prepared via acyl chloride **14** in the same manner as for cetyl ester **8b**. Esters **8c–f** have decreasing chain lengths from octyl **8c**, isoamyl **8d**, butyl **8e**, tert-butyl **8f** and isopropyl **8g**. It was found that the octyl and isoamyl esters **8c,d** produced soluble homopolymers (**9c,d**) that remained soluble throughout polymerisation reactions, whereas the smaller butyl and propyl esters (**8e–g**), were more problematic with a gel forming during the polymerisation. When this gel formed, it was clear by 1H-NMR spectroscopy that not all of the monomer had been consumed, and that monomers **8e–g** were therefore not suitable substrates for living polymerisations under the reaction conditions used. It was not possible to obtain molecular weight data by SEC for polymers **9e–g** due to their poor solubility. In contrast polymers **9c,d** could be characterised by SEC (Table 2).

For the soluble homopolymers (**9b–d**), thermal analysis (Table 2) revealed that that the materials are very thermally stable, with 10% mass loss not occurring until over 360 °C in each case (Figure 4). For the cetyl homopolymer **9b**, no glass transition temperature (Tg) was observable by differential scanning calorimetry, but a distinct crystallisation temperature (Tcryst) was observed in the cooling cycle. For isoamyl derivative **9d**, only a Tg was observed with no crystallisation, and both Tg and Tcryst were observable for octyl ester **9c**.

Having explored the use of long chain primary alcohols **13b–d**, long chain tertiary ester **8h** was prepared. Ester **8h** is derived from the naturally occurring terpene (*R*)-linalool **15** by hydrogenation to give (*S*)-4H-linalool[[35]](#endnote-36) **13h** followed by reaction with acyl chloride **14** (Scheme 3). Ester **8h** was

**Table 2:** Molecular weight and thermal analysis data for homopolymers **9b–d,h** (100:1 monomer : **10**).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Polymer** | **Mn (Da)** | **Mw (Da)** | **Đ** | **Tg (°C)** | **Tcryst (°C)** | **T10% (°C)** |
| **9d** (Isoamyl) | 14866 | 17136 | 1.15 | 101 | - | 365 |
| **9c** (Octyl) | 16121 | 18708 | 1.16 | 74 | 160 | 371 |
| **9b** (Cetyl) | 27735 | 28825 | 1.04 | - | 196 | 367 |
| **9h** (4H-linaloolyl) | 34467 | 40074 | 1.16 | - | - | 186 |



**Figure 4:** TGA traces of polymers **9b–d,h**.



**Scheme 3**: Synthesis of monomer **8h**.

polymerised to give homopolymer **9h**. This added a naturally derived, branched ester **8h** to the family of ester monomers **8** and illustrated that branched esters do not have a significant adverse impact on the polymerisation due to steric hindrance.

Molecular weight and thermal analysis data for homopolymer **9h** are included in Table 2. It is notable that polymer **9h** begins to decompose at a much lower temperature (T10% = 186 °C) than the other esters (Figure 4). The total mass loss below 300 oC (40%) corresponds exactly to that calculated for loss of the tertiary ester and reformation of acid **7**. This type of thermal elimination of tertiary esters is well precedented.[[36]](#endnote-37) As a result, for homopolymer **9h**, DSC was only possible over the range -60 °C to 165 °C, and no thermal features were observed.

Having established that a C5 ester is the minimum necessary for successful, living, homopolymerisation of substrates **8**, copolymer formation was investigated. Initially a mixture of the cetyl **8b** and methyl **8a** ester monomers was chosen as the most dissimilar of the monomer set to demonstrate compatibility. Monomers **8a** and **8b** were polymerised in a 50:50:1 **8a:8b**:**10** ratio to give a random copolymer **16** (Scheme 4) which SEC analysis (Figure 5) showed to be monomodal. Thermal analysis of random copolymer **16** showed a single glass transition temperature at 101 oC and the onset of decomposition at 369 oC.

Subsequently, attempts were made to grow a block copolymer comprising first of a block of cetyl ester monomer **8b**, then a block of methyl ester monomer **8a**. However, this turned out to be problematic as due to the long reaction time (3 days) required for the complete polymerisation of cetyl monomer **8b** it was difficult to judge the endpoint of this reaction and add the second monomer **8a** at the correct time.



**Scheme 4**: Random ROMP copolymerisation of monomers **8a** and **8b**.

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**Figure 5:** SEC trace for the copolymer formed from a 50:50:1 mixture of monomers **8a**, **8b** and catalyst **10**.

This resulted in highly bimodal molecular weight distributions. An attempt was also made to grow the same blocks in reverse order; polymerising first a block of the methyl ester **8a**, followed by a block of cetyl ester **8b**. However, the low solubility of the methyl ester polymer **9a** presented problems, with some material precipitating from solution, and full conversion of monomer **8a** was not achieved. Therefore, although cetyl monomer **8b** did polymerise onto the chains of polymer **9a** and produce some copolymer, the second block of this copolymer will consist of a random copolymer composed mostly of cetyl ester **8b** in combination with a small amount of monomer **8a** left over from formation of the initial block. Some insoluble material also remained after the growth of the second block, which suggests that the solubility of the methyl ester block was sufficiently poor that for some chains, polymerisation of the second block did not occur.

In order to overcome these limitations, an NMR study of the copolymerisation of monomers **8a** and **8b** was undertaken. Thus, a short block of seven equivalents of methyl ester **8a** followed by 25 equivalents of cetyl ester **8b** was polymerised in deuterated dichloromethane in a Youngs NMR tube



**Scheme 5**: ROMP block copolymerisation of monomers **8b** and **8a**.

(Scheme 5) and the polymerisation monitored by 1H NMR spectroscopy (at 298 K) over 42 hours. The resulting NMR spectra provided a wealth of information about the polymerisation. Figure 6 shows the changes observed in the alkene region of the NMR spectra over the course of the experiment, whilst Figures 7 and 8 highlight changes in the alkylidene region following the addition of monomers **8a** and **8b** respectively.

In Figure 6, the alkene signals of monomers **8a** and **8b** occur between 6.4 and 6.7 ppm. During the growth of the first block of the polymer, these peaks transform into broad signals at 5.7 to 6.1 ppm which correspond to the alkenes within the polymer and which gradually increase in intensity during the polymerisation. After 25 hours, monomer **8b** dissolved in additional deuterated dichloromethane was added, resulting in an increase in the intensity of the monomer alkene peaks and an apparent decrease in the intensity of the polymer alkene peaks due to dilution of the reaction mixture. Over the next 17 hours, the polymer alkene signals again increase in intensity, showing that monomer **7b** is being polymerised.

Figure 7 shows the alkylidene region of the 1H NMR spectra

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**Figure 6:** 1H NMR spectra (at 298 K) recorded every 20 min. of the ROMP of monomers **8a** and **8b**, showing the alkene region, indicating the consumption of monomer **8a**, then the addition of monomer **8b** (after 25 h.) and its continued ROMP.

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**Figure 7:** **:** 1H NMR spectra at 298 K of the ROMP of monomer **8a** showing the changes in the alkylidene region during the first 14 hours of the reaction.

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**Figure 8:** 1H NMR spectra at 298 K of the ROMP of monomers **8a** and **8b** showing the changes in the alkylidene region on addition of monomer **8b**.

(15-20 ppm). The signal at 19.1 ppm corresponds to catalyst **10** and can be seen to exponentially decay over a period of six hours showing that complete initiation of growing polymer chains occurs. The disappearance of the signal at 19.1 ppm, correlates with the initial appearance of a new alkylidene signal at 15.5 ppm, which also then decays away. The signal at 15.5 ppm can be assigned to the propagating alkylidene signal corresponding to the insertion of the first monomer unit into catalyst **10**. As the polymerisation progresses, the signal at 15.5 ppm transforms into a pair of signals at 15.4 ppm. The more downfield of these is also transient in nature and appears to correspond to the propagating alkylidene of the second monomer insertion product, whilst the more upfield of the two signals grows in intensity throughout the 25 hours of the first block of the co-polymerisation and corresponds to the living alkylidene signal of longer oligomers. The continued presence of this alkylidene signal and the absence of any other signals in the alkylidene region of the NMR spectra are testament to the well-controlled living nature of the ROMP of monomer **8a**. Integration of all the alkylidene signals present in the polymerisation showed no decrease with time, providing

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**Figure 9:** SEC trace for the copolymer formed from a 7:25:1 ratio of monomers **8a**, **8b** and catalyst **10**.

further evidence for the absence of termination reactions during the polymerisation.

Figure 8 shows an expansion of the propagating alkylidene region starting 25 hours into the polymerisation when monomer **8b** was added. The signal at 15.385 ppm corresponds to the most upfield signal in Figure 7, ie to the propagating alkylidene of poly-**8a**. Over the next five hours, this peak disappears and two new peaks at 15.355 and 15.350 ppm appear. The downfield of these is transient, whilst the upfield peak grows steadily in intensity over the next 17 hours. These two new peaks can be assigned to the first (15.355 ppm) and subsequent insertions of monomer **8b** onto the block of poly-**8a**. The fact that the signal at 15.385 ppm disappears as the peaks at 15.355 and 15.350 ppm appear is evidence that the polymerisation is giving a block copolymer, and not just two separate homopolymers of **8a** and **8b**.

This NMR experiment indicated that block copolymers of monomers **8** can be prepared, despite the slow rate of polymerisation, provided that the reaction is carefully monitored and the second monomer added slightly prior its being fully consumed to ensure that back-biting does not occur. The polymerisation was therefore repeated and the polymer isolated to give a polymer which SEC showed to be monomodal and to have a polydispersity of 1.08 (Figure 9). The 1H NMR spectrum of the polymer showed the presence of repeat units derived from both **8a** and **8b** in a 7:25 ratio.

In addition, it was possible to extract kinetic data from the signal intensities shown in Figures 7 and 8. Thus, the decrease in concentration of catalyst **10** was found to be first order (Figure 10) and allowed the rate of initiation of the polymerisation of monomer **8a** (ki**8a**) to be determined as 1.76 x 10-4 s-1 at 298 K. This value compares well with the value of 1.4 x 10-4 s-1 previously determined for initiation of other metathesis reactions in dichloromethane at 298 K using catalyst **10**.[[37]](#endnote-38),[[38]](#endnote-39) This is to be expected as the rate determining step of metathesis initiation by complex **10** is known to be dissociation of its tricyclohexylphosphine ligand, a process which is independent of the alkene to be metathesised.[[39]](#endnote-40)



**Figure 10:** First order kinetic plots for the determination of ki**8a** (red), kp**8a** (blue) and kp**8b** (green). To allow all three datasets to be plotted on the same graph, the start time for collection of kinetic data has been set to t=0 for each dataset.

Similarly, the increase in concentration of poly-**8a** (starting 5 hours into the polymerisation when all catalyst **10** has been consumed) could also be fitted to first order kinetics and gave an observed rate of propagation for the polymerisation of monomer **8a** at 298 K (k1obsp**8a**) as 2.2 x 10-5 s-1.‡ Thus, the rate of initiation of monomer **8a** is eight times faster than the rate of propagation which is consistent with the formation of polymers with narrow polydispersities. The observed rate of propagation for the polymerisation of monomer **8b** onto the block of poly-**8a** could be determined from the data in Figure 8 and was also found to fit first order kinetics (Figure 10) with k1obsp**8b** = 4 x 10-6 s-1 at 298 K.‡ This is 5.5 times smaller than k1obsp**8a** which may reflect additional steric hindrance within monomer **8b** due to the long alkyl ester.

Conclusions

Monomers **8a-h** constitute a new class of monomers for ring-opening metathesis polymerisation (ROMP) and which in some cases are fully bio-derived. The polymerisation of monomers derived from alcohols containing 1-4 carbon atoms gives polymers which are insoluble in common organic solvents, whilst ROMP of esters derived from alcohols containing five or more carbon atoms gives soluble polymers. In the latter cases, the polymerisations are shown to be well controlled living polymerisations, leading to polymers with narrow molecular weight distributions. Polymers derived from primary alcohols show high thermal stability, with no mass loss below 300 oC. In contrast, a polymer obtained from hydrogenated (*R*)-linalool, a tertiary alcohol, lost 40% of its mass (corresponding to the mass of the ester) between 180 and 300 oC. An NMR study of block copolymer formation between monomers **8a** and **8b** allowed multiple insertion products to be detected at the start of the polymerisations and gave kinetic data on the rates of initiation and propagation. Both random and block copolymers could be prepared with narrow molecular weight distributions. Ongoing work is focussed on extending the scope of monomers derived from acid **7** and related oxa-norbornene derivatives to give substrates which undergo more rapid ROMP with ruthenium based metathesis initiators such as complex **10**.

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    **Graphical Abstract:**

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