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Abstract: Ring-Opening Metathesis Polymerization (ROMP) of bio-based oxanorbornene amides by Grubbs second generation catalyst was used to prepare a range of well-defined homo- and co-polymers. A series of eleven amide monomers, featuring a variety of functionalities including amino acids and peptides, have been synthesized from a bio-based oxanorbornene acid, prepared through the 100% atom economical tandem Diels-Alder lactonization between itaconic anhydride and furfuryl alcohol. The polymerization has been shown to be well-controlled, with

the prepared homo- and co-polymers possessing controlled molecular weights with narrow polydispersities.

Introduction

Synthetic polymers have become ubiquitous in modern society, finding widespread application in packaging, building materials and consumer products, to name but a few. Consequently, there is a growing demand for these materials, with synthetic polymers currently produced on a scale of more than 300 million metric tonnes annually, the vast majority of which are derived from non-renewable petrochemical feedstocks.[1] This accounts for approximately 8% of the global crude oil and gas production, the second largest sector behind transport fuels.[2] However, fluctuating petroleum prices and environmental concerns, pertaining to their depletion, is driving interest in the production of synthetic polymers from renewable and sustainable resources. Currently only 1.7 million metric tonnes (ca. 0.57%) of synthetic polymers can be regarded as bioderived.[3] However, predictions suggest that 90% of the current total consumption of plastics could be replaced with bio-based alternatives.[1] A particular challenge is the synthesis of nitrogen containing bio-derived polymers as there are limited numbers of suitable nitrogen containing precursors with amino acids being the most readily available. The incorporation of nitrogen functionalities into polymers is however important as it can dramatically change the physical and chemical properties of the polymer. Polyamides such as Nylon and polyurethanes are examples of commercially important nitrogen-containing synthetic polymers. Nitrogen functionality in monomers can also cause problems during polymerizations as the Brønsted or Lewis basicity associated with functional groups such as amines and amides can result in inhibition or decomposition of polymerization initiators.

There are generally two distinct approaches for the preparation of bio-based plastics. Either the development of sustainable routes to monomers chemically equivalent to those derived from petrochemical sources (bioreplacement), or the synthesis of novel structures from biomass as new sustainable monomer species (bioadvantage).[4] We had previously been interested in the development of aromatic itaconate esters, with the intention of producing bio-based furan analogues of poly(benzyl)itaconiates, through radical polymerization.[5,6,7,8] It was expected that these would possess higher glass transition temperatures (T_g) than their poly(dialkyl)itaconate equivalents.[9] However, the reaction between itaconic anhydride **1** and furfuryl alcohol **2** gave not ester **3**, but the unusual oxanorbornene-lactone **4** as a single product (Scheme 1).[10] This outcome was reported independently and simultaneously by Pehere *et al.*[11]
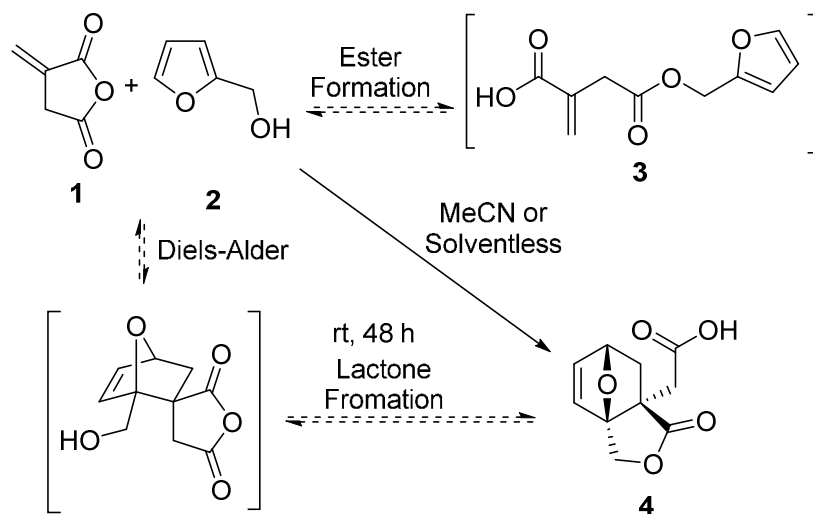
Scheme 1. Preparation of acid **4**.

The formation of acid **4** occurs *via* a tandem Diels-Alder cycloaddition followed by lactone formation. Diels-Alder reactions of furans are reversible and in this case, subsequent

lactonization causes product **4** to precipitate from the reaction mixture. This reaction is effective when carried out both with a solvent, usually acetonitrile, or under solvent free conditions. As such, compound **4** is a very promising candidate for the development of sustainable polymers, as its synthesis from compounds **1** and **2** is 100% atom economical and can performed without the need for solvents, catalysts or other reagents. Additionally, both starting materials (**1** and **2**) are highly promising platform molecules for a bio-economy and are currently produced on an industrial scale.[12] Alcohol **2** is readily available by the hydrogenation of furfural[13] **5** (Figure 1) which is produced by the acid catalyzed dehydration of pentoses (ca. 200 000 tons per annum), usually from agricultural waste.[14,15] Itaconic acid **6** can be obtained by fungal fermentation carbohydrates using *Aspergillus terreus* (ca. 400 000 tons per annum by 2020).[16] However, anhydride **1** is most efficiently made, not from itaconic acid **6**, but from citric acid **7**, which undergoes simultaneous decarboxylation and dehydration to yield itaconic anhydride **1** directly when distilled.[17] Citric acid is produced on over a one million tons per annum scale by fermentation of glucose-containing sugars with *Aspergillus niger*, making it an equally sustainable feedstock.[18]
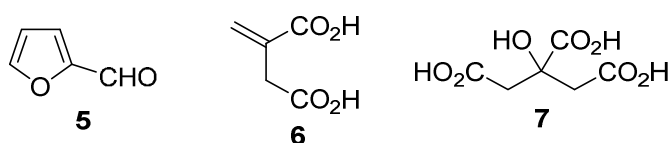
Figure 1. Structures **5-7**.

As a result of significant advances in initiator activity and functional group tolerance, ROMP has developed into a versatile methodology for the synthesis of highly functionalized polymers with controlled molecular weights and stereochemistry.[19,20,21] Ruthenium based ROMP initiators

have also been used to polymerize monomers which incorporate natural products within their structures.[22,23,24,25,26,27] In previous work we have shown that esters of acid **4** could be polymerized by ROMP in the presence of Grubbs second generation catalyst **G2** (Scheme 2).[10,28]
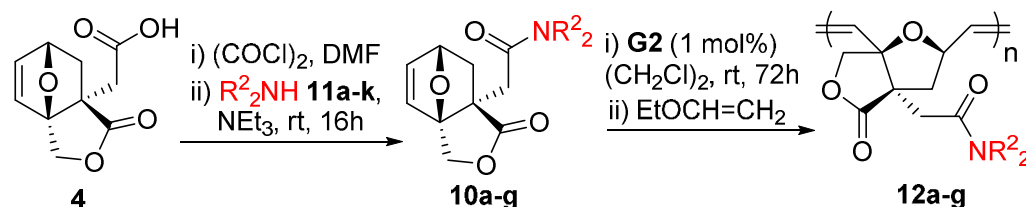
Scheme 2. ROMP of esters **9a-h** and amides **10a-k**.

The homopolymer **8a** of methyl ester **9a** was found to have poor solubility in a range of solvents, but monomer **9a** did undergo well-controlled polymerization to give soluble copolymers when

copolymerized with a commercial norbornene derivative. To increase the solubility of the homopolymers, esters **9b-h** were subsequently prepared, most of which can be obtained from bio-mass derived alcohols.[28] Esters **8b-h** were found to undergo ROMP over 72 hours in a well-controlled manner, to give wholly biomass derived homo- and co-polymers. The polymers were produced with narrow polydispersities, and in most cases, were found to possess good thermal stability. Consequently, we have been interested in further functionalization of oxanorbornene-acid **4** and in the properties of the corresponding polymers obtained by ROMP. Herein, we demonstrate that acid **4** can be converted into a range of tertiary amides **10a-k**, including those derived from amino acids and peptides, and that the resulting amides also undergo well-controlled ROMP to form nitrogen containing polymers.

Experimental

Details of materials, reagents and analytical methods are given in the supporting information.

General Procedure for the Synthesis of Amides 10a-k:

Acid monomer[10] **4** (2.0 g, 9.5 mmol) was suspended in anhydrous CH_2Cl_2 (5 mL) under an argon atmosphere. The suspension was cooled to 0 °C and oxalyl chloride (12.0 mL of 2.0 M solution in CH_2Cl_2, 24.0 mmol) was added dropwise over 10 minutes, followed by DMF (4 drops). The suspension was stirred at ambient temperature until a solution was obtained. The obtained solution was concentrated *in vacuo*, to give a brown solid which was redissolved in anhydrous CH_2Cl_2 (10 mL) and cooled to 0 °C. A solution of disubstituted amine **11a-k** (14 mmol) and triethylamine (2.7 mL, 19.0 mmol) (or 5.4 mL, 38.0 mmol if using the TFA salt of amine **11**) in CH_2Cl_2 (10 mL) was added dropwise over 10 minutes. The solution was allowed to

stir at ambient temperature overnight, then additional CH_2Cl_2 (30 mL) and H_2O (50 mL) were added. The organic layer was separated and further washed with 1M HCl_{aq} (50 mL), 1M $NaHCO_3$ (50 mL), H_2O (50 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was then purified using flash column chromatography. Details of solvent systems and compound characterization are given in the supporting information.

General Procedure for the ROMP of Amides 10a-k:

The appropriate quantities of monomer(s) and catalyst **G2** were separately dissolved in $(CH_2Cl)_2$. Each solution was degassed by three cycles of freeze-pump-thaw. The monomer solution was prewarmed to the desired temperature and the catalyst solution added. The reaction mixture was then stirred for 72 h. After this time, the polymerization was terminated by the addition of an excess of ethyl vinyl ether, followed by stirring for a further 30 minutes. The solution was then filtered through a short plug of silica to remove catalyst residues. The solution was then precipitated into hexane. After settling, the hexane was carefully decanted and the polymer dried under reduced pressure. Details polymer characterization are given in the supporting information.

Procedure for the Synthesis of Dibenzyl/Diethyl Block Copolymer

Dibenzyl amide **10g** (39 mg, 0.1 mmol) and catalyst **G2** were combined in a Schlenk tube under argon. $(CH_2Cl)_2$ was degassed by three cycles of freeze-pump-thaw, then $(CH_2Cl)_2$ (1 mL) was added to the Schlenk tube containing the monomer/catalyst. The reaction mixture was then stirred at 40 °C for 13.6 h, which corresponds to 80% conversion, as determined by the kinetic

plot obtained for monomer **10g**. After 13.6 h, a sample was taken and immediately analyzed by ^{1}H NMR spectroscopy to determine the conversion. A second sample was then taken, end-capped by treatment with excess ethyl vinyl ether for 30 minutes, filtered through a silica plug and precipitated into hexane. The hexane was decanted and the sample dried under reduced pressure before being analyzed by SEC. A solution of diethyl monomer **10b** (29 mg, 0.1 mmol) in $(CH_2Cl)_2$ (1 mL), which had been subjected to degassing by three cycles of freeze-pump-thaw, was then added to the reaction mixture. The reaction was monitored by SEC and ^{1}H NMR spectroscopy every 24 h for the next 48 h as the second block was incorporated according to the previously described procedure. After 48 h the polymer was end-capped by treatment with excess ethyl vinyl ether for 30 minutes. The polymer was then filtered through a plug of silica and precipitated into hexane. The hexane was decanted and the polymer dried under reduced pressure before being analyzed by ^{1}H NMR spectroscopy and SEC. Details polymer characterization are given in the supporting information.

General Procedure for Monitoring the Kinetics of Amide Homopolymerization

The appropriate quantities of monomer(s) and catalyst **G2** (1.7 mg, 1 mol%) were separately dissolved in $(CD_2Cl)_2$ (0.5 mL). Tetramethylsilane (1 drop) was then added to the monomer solution. Each solution was subjected to three cycles of degassing by freeze-pump-thaw. The monomer and catalyst solution were then combined. A sample of the reaction mixture was then transferred to an NMR tube equipped with a Young tap. The sample was sealed under argon and ^{1}H NMR spectra recorded at 40 °C every 30 mins for 24 h. Conversion was then determined by integrating monomer alkene peaks relative to the TMS peak.

Results and Discussion

Acid **4** was converted into its acid chloride as previously reported,[28] then reacted with disubstituted amines **11a-k** to give tertiary amide monomers **10a-k** (Scheme 2). The structures of amides **10b,g** and **h** were confirmed by X-ray crystallography (Figure 2). The eventual aim of this project was to use bio-based amines to complement the 100% bio-derived nature of acid **4**. However, bio-based amines are rather scarce and can only be easily obtained from chitin or amino acids.[29] Alternative approaches have typically resorted to amination of bio-based platform molecules.[30,31] Therefore, initial studies to prove that amide containing monomers would undergo ROMP were carried out using simple petrochemically derived amines **11a-g**, to produce the corresponding tertiary amides **10a-g**, in good to excellent yields.
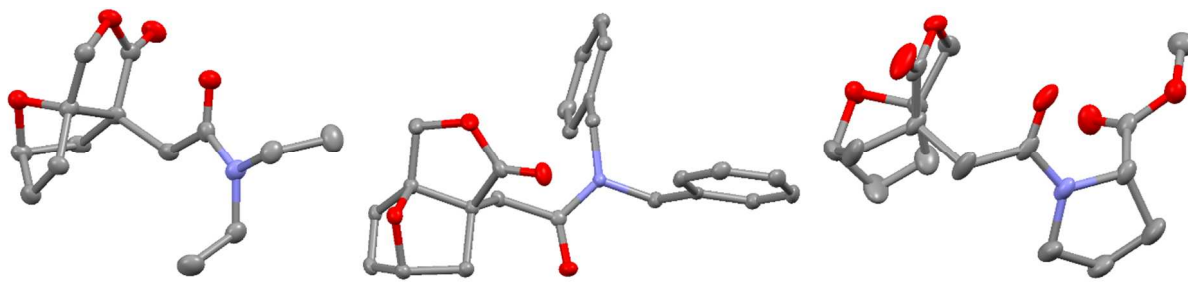
Figure 2: Elipsoid representations of the crystal structures of monomers **10b**,**g** and **h**. The tetrahydropyrrole and butyrolactone of **10h** were disordered and only the major form of each is shown.

Alternative routes to the synthesis of amide **10g** were also investigated to avoid the use of oxalyl chloride and chlorinated solvents. However, attempts to prepare the amide directly from acid **4** and amine **11g** using amorphous or mesoporous (SBA15) silica[32] activated at 700 $^{\circ}$C, or

boric acid,[33] as catalysts in refluxing toluene were unsuccessful and resulted in the decomposition of acid **4**.

ROMP conditions were then optimized using the dibenzyl amide **10g** as model substrate. Polymerizations to form homopolymer **12g** were attempted using 1 mol% of catalysts **G1-G3** (Figure 3), in 1,2-dichloroethane at various temperatures and concentrations for 72 hours, after which time a sample was taken and analyzed by ^{1}H NMR spectroscopy to determine conversion. The polymerization was then quenched with ethyl vinyl ether and the resulting polymer was analyzed by SEC (Table 1). 1,2-Dichloroethane was chosen as the solvent as it had given the best results for the ROMP of esters **9a-h**.[10,28] When polymerization was performed at room temperature using catalyst **G2** and a 0.1 M concentration of monomer **10g**, identical conditions to those previously used for the ester derivatives,[10,28] only 37% conversion was observed (Table 1, entry 1). Performing the polymerization at elevated temperature had a positive influence on the conversion, with 82% of monomer **10g** converted at 30 °C (Table 1, entry 2) and 91% of monomer converted at 40 °C (Table 1, entry 3). Above 40 °C, there was no significant further improvement in the conversion (Table 1, entries 4 and 5). Reducing the polymerization temperature to 0 °C completely suppressed the polymerization of monomer **10g** (Table 1, entry 6). The molecular weight of polymer **12g** increased as the conversion increased as expected for a well-controlled ROMP and the use of elevated polymerization temperatures did not have a significantly detrimental effect on the dispersity of polymer **12g** with all samples displaying polydispersities below 1.1 (Table 1, entries 1-4). The temperature dependence of the polymerization of monomer **10g** is consistent with the known need to dissociate the tricyclohexylphosphine ligand from **G2** as the rate determining step of metathesis initiation with

this catalyst.[34] This will be an endothermic process and hence will be facilitated at elevated temperatures.

Mes = 2,4,6-Trimethylphenyl; Cy = cyclohexyl
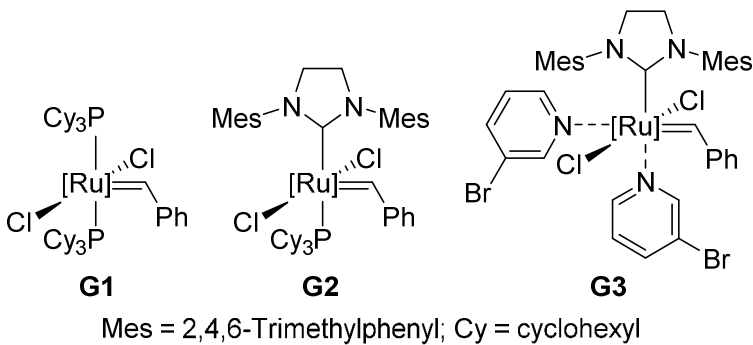
Figure 3: Structures of metathesis catalysts **G1-G3**.

Table 1. Reaction optimization for the ROMP of dibenzyl amide **10g**.[a]

Entry	Catalyst	Temperature (°C)	[10g] (M)	Conversion (%)[b]	M_n[c]	M_w[c]	Đ[d]
1	G2	rt	0.10	37	16,100	17,000	1.06
2	G2	30	0.10	82	18,500	19,100	1.03
3	G2	40	0.10	91	20,400	21,400	1.05
4	G2	50	0.10	93	23,500	25,100	1.07
5	G2	60	0.10	93	22,000	23,500	1.07
6	G2	0	0.10	0			
7	G2	40	0.05	79	17,800	19,000	1.06
8	G2	40	0.20	91	16,900	17,700	1.05
9	G1	rt	0.10	0			
10	G1	40	0.10	0			
11	G3	rt	0.10	0			
12	G3	40	0.10	0			

a) All polymerizations were carried out using a **10g**:catalyst ratio of 100:1. b) Conversion was determined by ^{1}H NMR spectroscopy. c) Determined by SEC in THF at 23 °C and calibrated relative to polystyrene standards. d) Đ = M_w/M_n.

Halving the concentration of monomer **10g** decreased the conversion (Table 1, entry 7), but doubling its concentration did not increase the conversion (Table 1, entry 8). Attempts to polymerize monomer **10g** using first or third generation Grubbs catalysts (**G1** and **G3**) were unsuccessful (Table 1, entries 9-12). Thus, the use of catalyst **G2** (initially 1 mol%) with a 0.1 M solution of monomer in 1,2-dichlorethane at 40 °C for 72 h were chosen as the conditions to further study the polymerization of monomers **10a-k**. under these conditions the homopolymerization of dibenzyl amide **10g** was repeated at **10g:G2** ratios of 20:1 to 100:1 (Table 2). In each case polymer **12g** was obtained with narrow polydispersity (Figure 4) and there was a linear relationship between the number averaged molecular weights and the **10g:G2** ratio (Figure 5) which is indicative of the homopolymerization of monomer **10g** being a well-controlled chain growth polymersation.

Table 2. Molecular weight data for homopolymers **12g** of dibenzyl amide **10g**.

Entry	**10g**:**G2**	M_n[a]	M_w[a]	Đ[b]
1	20:1	8,400	8,900	1.06
2	40:1	14,100	14,900	1.05
3	60:1	18,400	19,600	1.06
4	80:1	23,100	25,100	1.09
5	100:1	26,200	28,900	1.10

a) Determined by SEC in THF at 23 °C and calibrated relative to polystyrene standards. b) Đ = M_w/M_n.
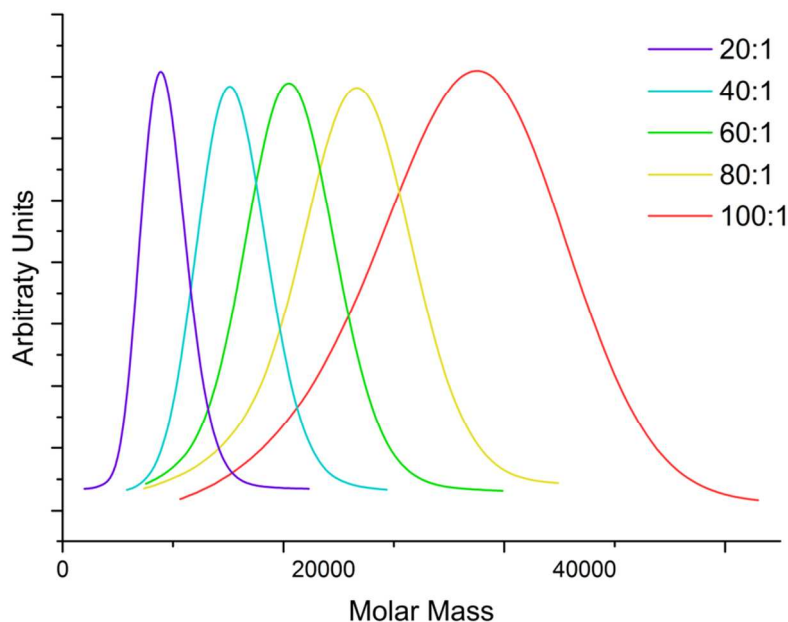
Figure 4. SEC of homopolymer **12g** prepared using various **10g:G2** ratios.
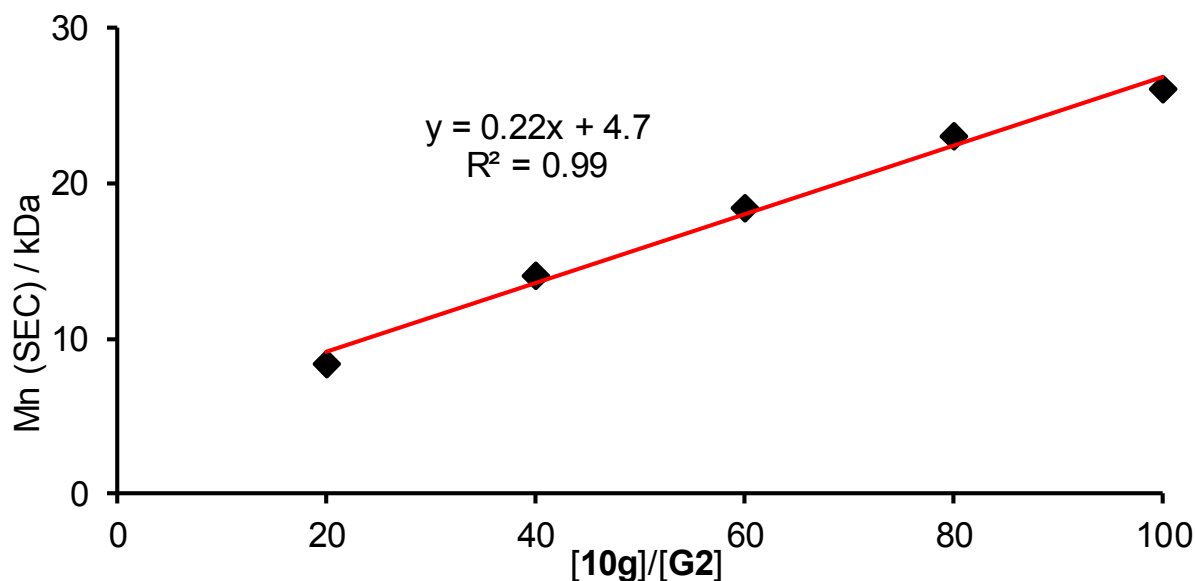

$$y = 0.22x + 4.7$$
$$R^2 = 0.99$$

Figure 5. Plot of M_n against **10g:G2** ratio for homopolymer **12g**.

Having demonstrated using monomer **10g** that ROMP of tertiary amide derivatives of

oxanorbornene **4** was possible and occurs in a well-controlled manner, a series of homopolymers

12a-k were prepared using amides **10a-k** (Table 3). Generally, the polymers were obtained with molecular weights close to the expected values and with narrow polydispersities. Polymers **12a,b** could not be analyzed by SEC as they were insoluble in THF (Table 3, entries 1 and 2). As these polymers are derived from monomers with the shortest alkyl chains (Me and Et), this suggests that more than four carbon atoms need to be present in the amide unit for the polymers to be soluble in organic solvents. This is consistent with our previous experience of homopolymers **8a-h** derived from ester containing monomers **9a-h**.[28]

Soluble polymers with molecular weights close to the expected values were obtained for the homopolymers **12c,d** of propyl and butyl amides **10c,d** (Table 3, entries 3 and 4). However, monomers **10e,f** which have longer linear or branched alkyl groups on the amide seem to inhibit the polymerization (Table 3, entries 5 and 6). This is apparent in the conversions obtained for the polymerization of monomers **10e,f** after 72 hours and, for polymer **12f**, in the much lower than expected number average molecular weight. However, monomers **10e,f** still gave polymers **12e,f** with narrow polydispersities. This effect seems to be restricted to larger aliphatic groups as monomer **10g** which contains two large, branched, benzyl groups underwent ROMP without any difficulty (Table 3, entry 7 and Tables 1 and 2).

Having shown that symmetrical tertiary amides **10a-g** derived from petrochemically sourced secondary amines **11a-g** all underwent ROMP, the use of monomers **10h-k** which all contain unsymmetrical tertiary amides derived from amino acids was investigated. Initially, acid **4** (racemic) was reacted with methyl (*S*)-prolinate to give amide **10h** as a 1:1 mixture of diastereomers. Monomer **10h** underwent ROMP under the standard conditions (Table 3, entry 8), but the resulting polymer was insoluble in THF. To avoid complications due to the presence of diastereomers when racemic acid **4** was coupled to chiral amines, it was decided to limit the

study to achiral amino acid derivatives. Thus, monomer **10i** derived from sarcosine (*N*-methylglycine) benzyl ester was prepared and cleanly converted into polymer **12i**, which SEC showed to have the right number average molecular weight and a narrow polydispersity (Table 3, entry 9).

Table 3: Molecular weight and thermal analysis data for homopolymers **12a-k**.[a]

Entry	Polymer	Conversion (%)[b]	M_n[c]	M_w[c]	Đ[d]	T_g (°C)	$T_{10\%}$ (°C)
1	**12a** (amide = NMe$_2$)[e]	93				115	345
2	**12b** (amide = NEt$_2$)[e]	90				146	349
3	**12c** (amide = NPr$_2$)	78	25,700	28,100	1.09	203	350
4	**12d** (amide = NBu$_2$)	82	25,000	26,800	1.07	139	361
5	**12e** (amide = NOct$_2$)	52	23,300	23,700	1.02	137	269
6	**12f** (amide = (2-ethylhexyl)$_2$)[e]	49	10,900	12,100	1.11	171	321
7	**12g** (amide = NBn$_2$)	91	20,100	21,000	1.04	130	352
8	**12h** (amide = Pro-OMe)[f]	87				149	332
9	**12i** (amide = Sar-OBn)	87	18,300	19,900	1.09		327
10	**12j** (amide = Sar-Gly-OBn)[f]	-[g]				155	306
11	**12k** (amide = Sar-Sar-OBn)[f]	62					315

a) All polymerizations were carried out in 1,2-dichloroethane at 40 °C for 72 hours using catalyst **G2** and a **10a-k**:**G2** ratio of 100:1. b) Conversion was determined by ^{1}H NMR spectroscopy. c) Determined by SEC in THF at 23 °C and calibrated relative to polystyrene standards. d) Đ = M_w/M_n. e) Amine **11f** was used as a mixture of racemic and meso-stereoisomers. f) Polymer was insoluble in THF. g) Conversion could not be determined as polymer precipitated out of solution over 72 hours.

The study was then extended to monomers **10j,k** derived from peptides, again using achiral amino acids to avoid complications caused by diastereomer formation. Previous work on ROMP of peptide derived norbornenes has been based on the potential of the polymers as functional materials and therapeutic agents.[35,36,37,38,39] Monomers **10j,k** differ only by the presence of a hydrogen (**10j**) or methyl group (**10k**) on the nitrogen of the *C*-terminal amino acid. In the case of monomer **10j**, the polymerization did occur, but the polymer precipitated from the reaction mixture as it was formed over the course of 72 hours (Table 3, entry 10). The polymerization of monomer **10k** was more straightforward (Table 3, entry 11), though both polymers **12j,k** were insoluble in THF and so could not be analyzed by SEC.

All of monomers **10a-k** contain a tertiary amide structure. The ROMP of analogous monomers containing a secondary amide unit was also investigated but in every case was unsuccessful. This is probably due to the *endo*-nature of the amide substituent which aids coordination of the amide to the propagating metal alkylidene, inhibiting catalyst turnover, in a similar manner to that previously observed by Sutthasupa *et al* and Lapinte *et al*.[40,41] This coordination would be stronger in the case of a secondary amide due to its ability to form an imidic acid tautomer. The formation of polymer from monomer **10j** does however show that secondary amides are compatible with ROMP initiated by catalyst **G2**, provided they are present far enough away from the alkene to disfavour their coordination to the propagating metal alkylidene.

The thermal properties of homopolymers **12a-k** were also determined, using TGA and DSC analysis (Table 3). The polymers were found to be amorphous, as no T_m or T_{cryst} was observed in any case, but showed fairly high T_g values ranging from 115-203 °C. The polymers also mostly displayed high temperatures of decomposition ($T_{10\%}$) with values typically obtained between 305-361 °C (Figure 6). The only exception was polymer **12e** derived from dioctylamine **11e**

which had a lower decomposition temperature of 269 °C. Samples of polymers **12i,j** showed a stepwise weight loss, losing 10-15% of the sample mass at 100-150 °C, before a second weight loss occurs above 300 °C. The higher temperature weight loss corresponds to polymer decomposition as for polymers **12a-h,k** and TGA-FTIR analysis showed that the lower temperature weight loss was due to release of encapsulated hexane. Encapsulation of hydrocarbons, including hexane, within polynorbornenes has been reported before[42] and is known to be highly dependent upon the exact structure of the monomer.
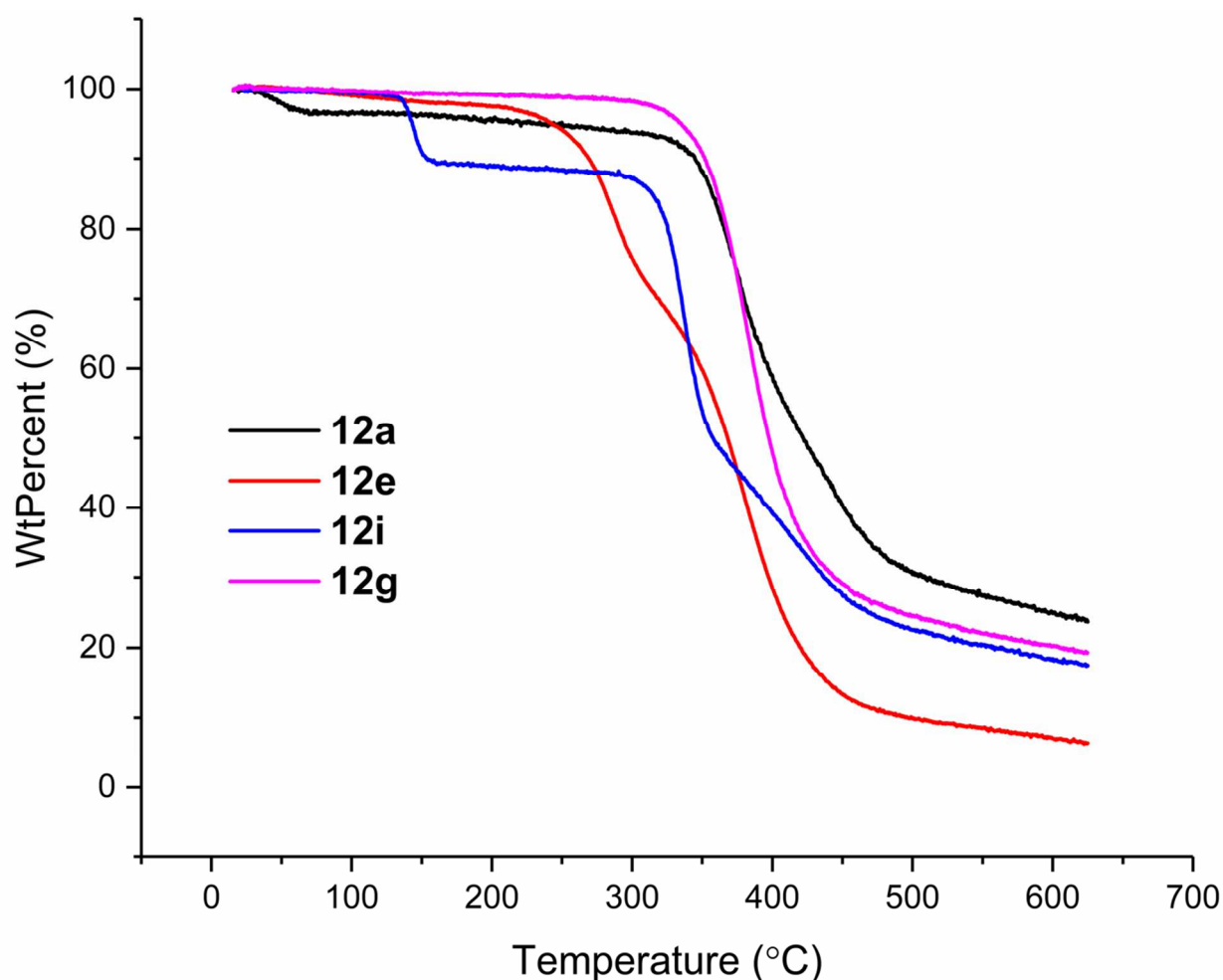

Figure 6: TGA traces for homopolymers **12a**,**e,g,i**.

Having studied the formation of homopolymers **12a-k** from monomers **10a-k**, the synthesis of random copolymers **13a-d** was investigated, focusing particularly on those monomers that had produced insoluble homopolymers (Scheme 3 and Table 4). Copolymers **13a-d** were all prepared from a 50:50:1 ratio of the two monomers to **G2**, to give copolymers which were comparable with homopolymers **12** prepared using a 100:1 monomer to **G2** ratio (Table 3). High conversions of monomers **10** to polymers **13a-d** was observed in all cases within 72 hours, to give polymers with narrow polydispersities (Figure 7). Polymer **13a** was derived from monomers **10c** and **10i** both of which had given soluble homopolymers (Table 3) and not surprisingly give a soluble random copolymer (Table 4, entry 1). The other three random copolymers prepared (**13b-d**) were all derived from one monomer which had given a soluble homopolymer and one which had given an insoluble homopolymer. Two of these combinations were found to give soluble copolymers (Table 4, entries 2 and 3), but the third gave a random copolymer that insoluble in organic solvents (Table 4, entry 4).
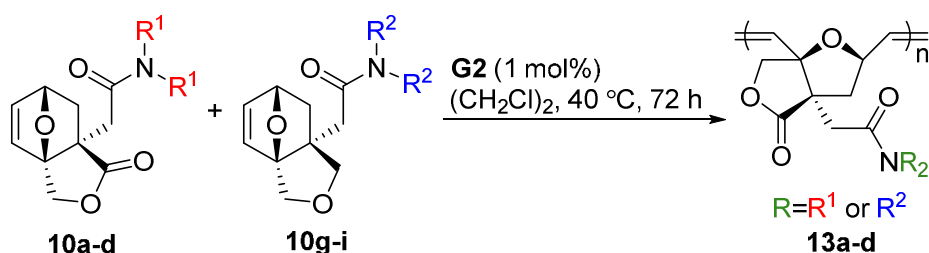
Scheme 3: Random ROMP copolymerization of monomers **10**.

Table 4: Molecular weight and thermal analysis data for random copolymers **13a-d**[a]

Polymer (monomers)	Conversion (%)[b]	M_n[c]	M_w[c]	Đ	T_g (°C)	$T_{10\%}$ (°C)
13a (10c:10i)	80	10,800	12,000	1.11		319
13b (10b:10g)	89	25,100	27,500	1.10	157	355
13c (10d:10h)	89	12,200	12,900	1.06	155	307
13d (10a:10i)[d]	95					319

a) Polymerizations were carried out in 1,2-dichloroethane at 40 °C for 72 hours using catalyst **G2** and a monomer:catalyst ratio of (50:50:1). b) Conversion was determined by ^{1}H NMR analysis. c) Determined by SEC in THF at 23 °C and calibrated relative to polystyrene standards. d) Polymer was insoluble in THF.

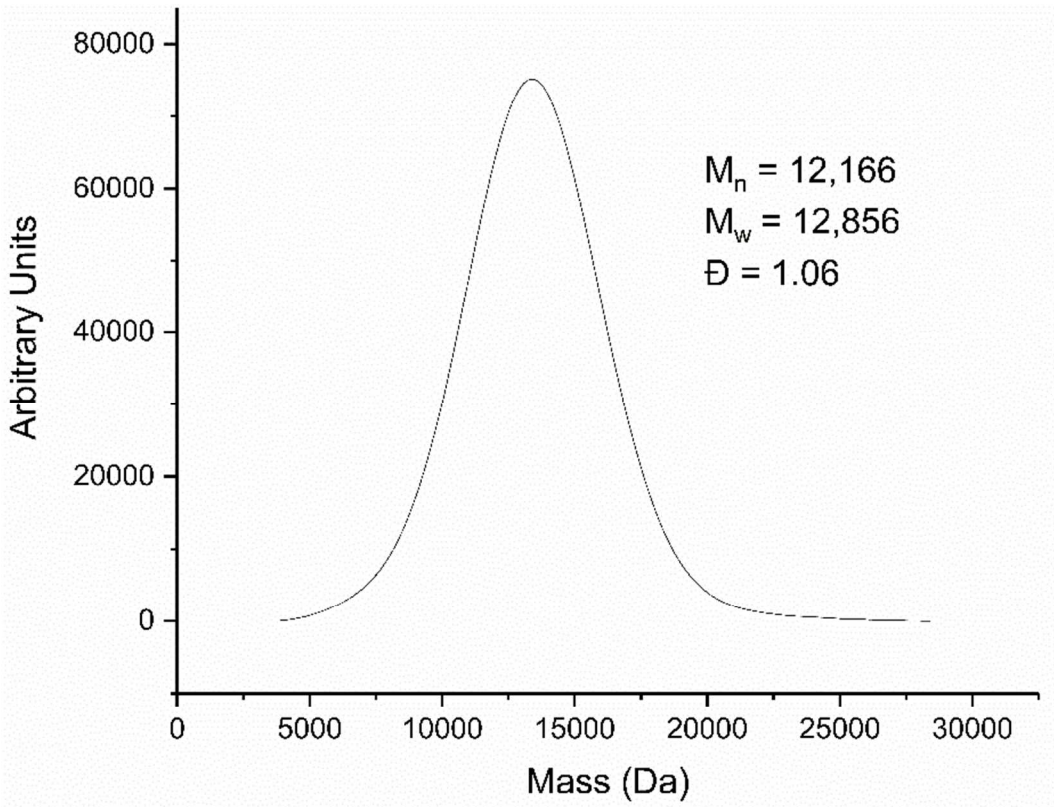
$M_n = 12,166$
$M_w = 12,856$
$Đ = 1.06$

Figure 7: SEC trace for the copolymer formed from a 50:50:1 mixture of monomers **10d,h** and catalyst **G2**.

Thermal analysis of the random copolymers indicated that they possessed similar properties to the homopolymers. T_g values were only observed for copolymers **13b,c** but were fairly high at 157 and 155 °C respectively. Thermal decomposition temperatures were again above 300 °C, and polymer **13a** which included sarcosine benzyl ester **10j** as one of its monomers again showed hexane encapsulation, exactly analogous to that observed for homopolymer **12j**.

The synthesis of a block copolymer **14** using the benzyl **10g** and ethyl **10b** monomers was then undertaken by the sequential addition of monomers **10g** and **10b** (Scheme 4). Initial reactions gave bimodal SEC traces due to chain ends dying before the second monomer was added. The same effect had been observed for the preparation of block copolymers using catalyst **G2** with the analogous ester monomers.[28] This problem could be solved by monitoring polymerization of the first monomer, to ensure that the second monomer was added slightly prior to the first monomer being fully consumed. The homopolymerization of monomer **10g** was therefore monitored by ^{1}H NMR spectroscopy and SEC, to allow for a more accurate determination of the polymerization end-point. This showed that, 50 equivalents of monomer **10g**, was 80% consumed after 13.6 hours. After 13.6 hours, 50 equivalents of monomer **10b** was added, then the reaction was monitored every 24 hours before quenching after 48 hours. The resulting SEC traces (Figure 8) show that the both blocks produce monomodal high molecular weight polymer with narrow polydispersityand hence indicate that there were no issues with dead chain ends.
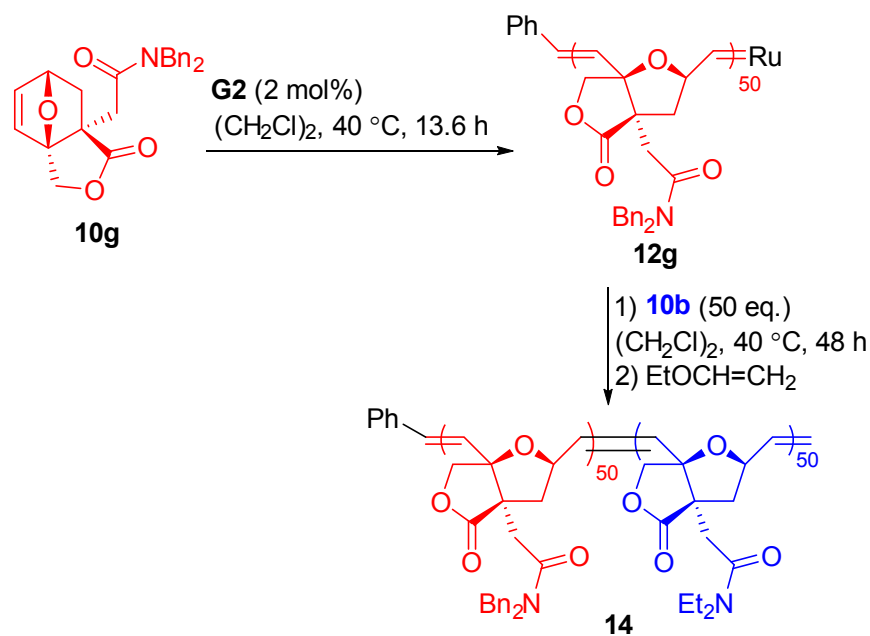
Scheme 4: Block copolymerization of monomers **10g** and **10b** to produce block copolymer **14**.
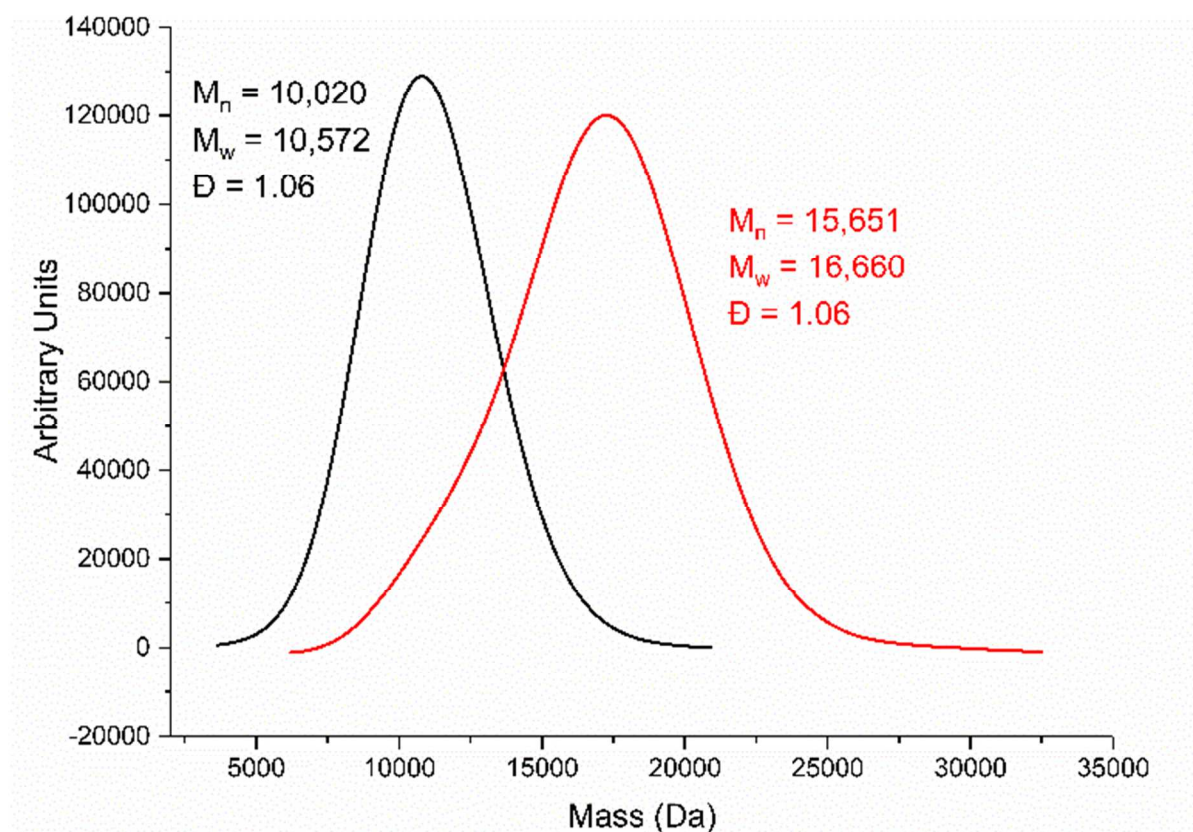

Figure 8: SEC trace for the block copolymer formed from 50:50:1 **10g**:**10b**:**G2**. Black, 13.6 hours after addition of monomer **10g**. Red 48 h after addition of monomer **10b**.

Monitoring the reaction profile by ^{1}H NMR also made it possible to determine kinetic information on the homopolymerization of these tertiary amides. The decrease in concentration of dibenzyl monomer **10g** against time was found to fit first order kinetics at 40 °C in deuterated 1,2-dichloroethane, giving an observed rate value (K_{obs}) of 2.1×10^{-3} s^{-1} when the natural logarithm of concentration was plotted against time (Figure 9). This study was then extended to monomers **10a,d,e** and **i**. Monomer **10a** (derived from dimethylamine) was found to have the highest observed rate constant (2.3×10^{-3} s^{-1}) whilst monomer **10e** (derived from dioctylamine) was found to have the lowest observed rate constant (3.1×10^{-4} s^{-1}). The relative small difference (a factor of eight) between the highest and lowest of these rate constants suggests that the structure of the amide substituents does not have a large effect on the rate of polymerization of monomers **10**.
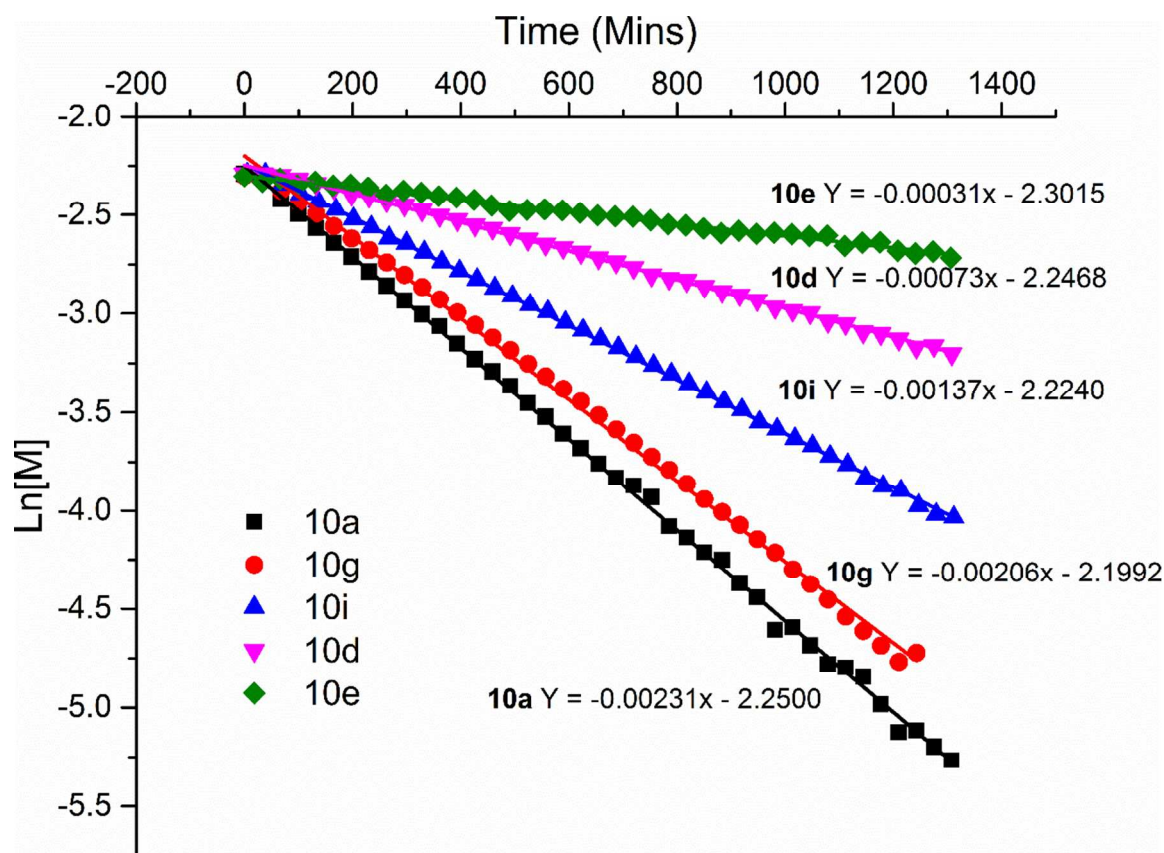

Figure 9: First order kinetic plots for the determination of K_{obs} for monomer **10a**,**d**,**g** and **i**

Conclusions

A series of eleven tertiary amide monomers have been synthesized from a bio-based oxanorbornene prepared from itaconic anhydride and furfuryl alcohol. ROMP of these tertiary amides was shown to procced in a well-controlled manner, producing a range of nitrogen containing homo- and random- copolymers with high molecular weights with narrow polydispersities. Thermal analysis showed that the polymers were amorphous with T_g values in the range of 115-203 °C and thermal decomposition temperatures typically above 300 °C. A block copolymer could also be prepared by monitoring the progress of the growth of the first polymer block to ensure that the second monomer was added before chain termination became significant. Monitoring the homopolymerizations also provided kinetic data on the rates of polymerization of the monomers.

ASSOCIATED CONTENT

Details of instrumentation, analytical methods, material and reagents as well as characterizing data and spectra for all monomers and polymers and kinetic plots are given in the supporting information. X-ray data for compounds **10b,g,h** have been deposited with the Cambridge crystal structure database and have reference numbers CCDC1823661, CCDC1823662 and CCDC1823663 respectively.

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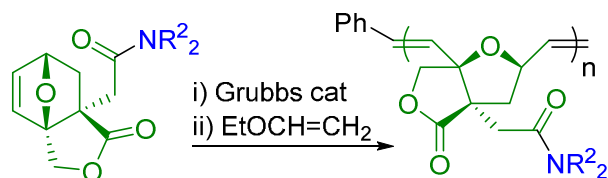
Synopsis

ROMP is used to prepare nitrogen containing polymers. The monomers can be prepared from sustainably sourced chemicals: itaconic acid, furfurol and amino acids.
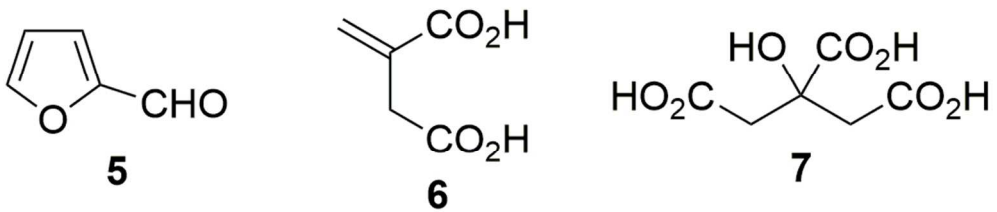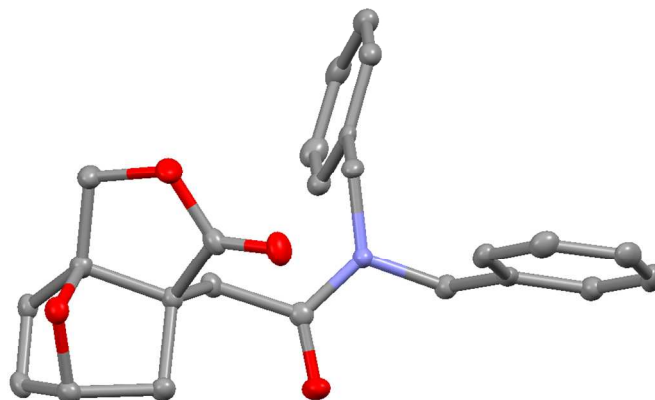
Figure 1

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Figure 2, center image
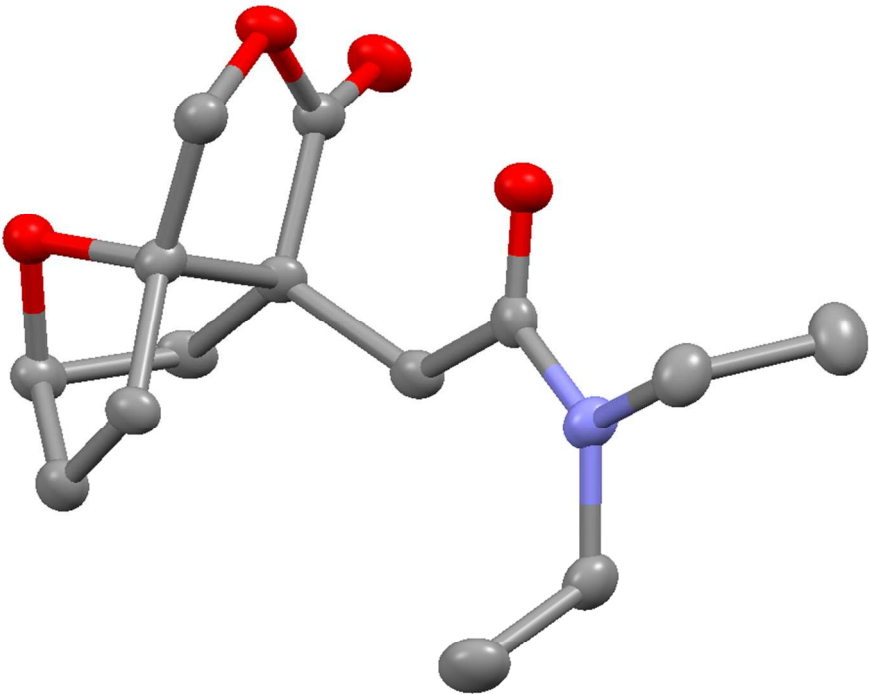
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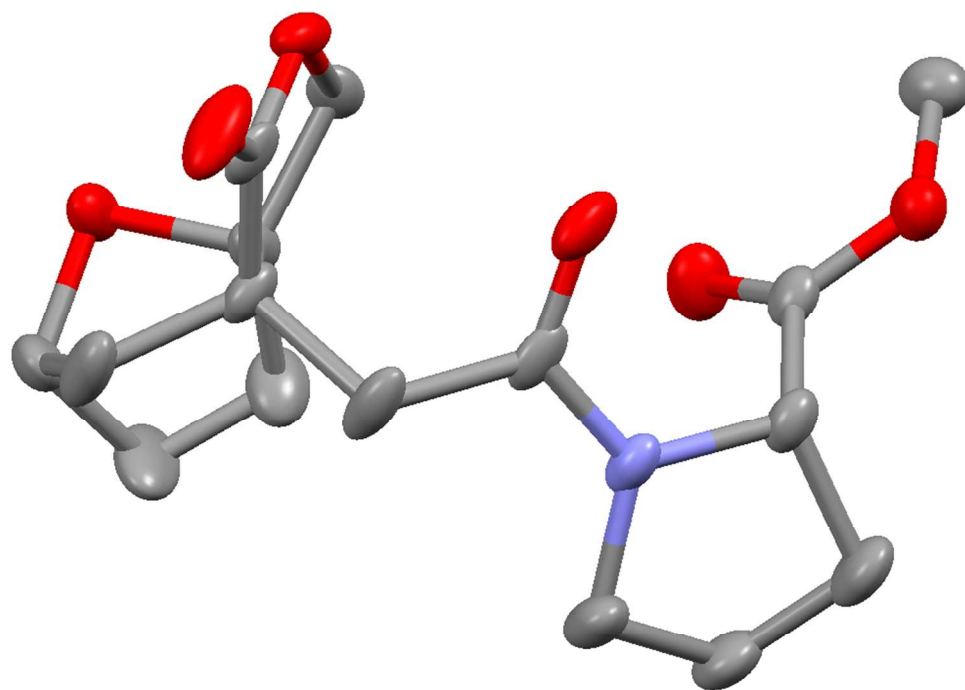
Figure 2, left image

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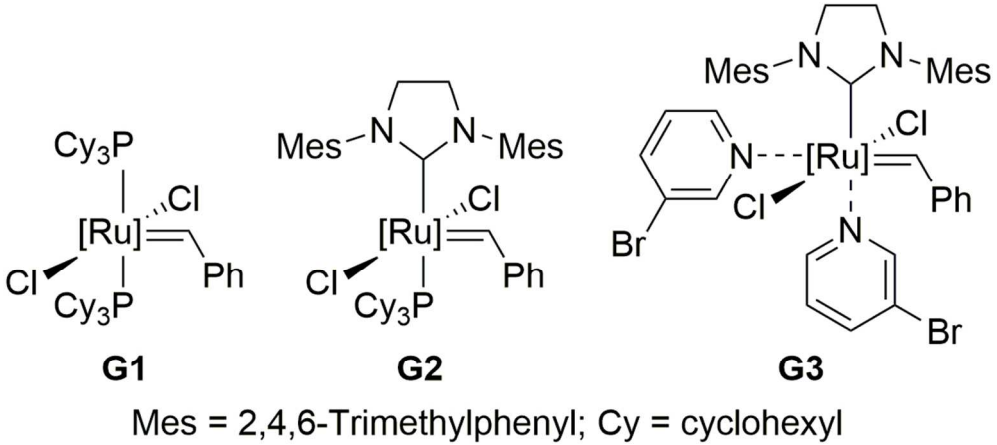
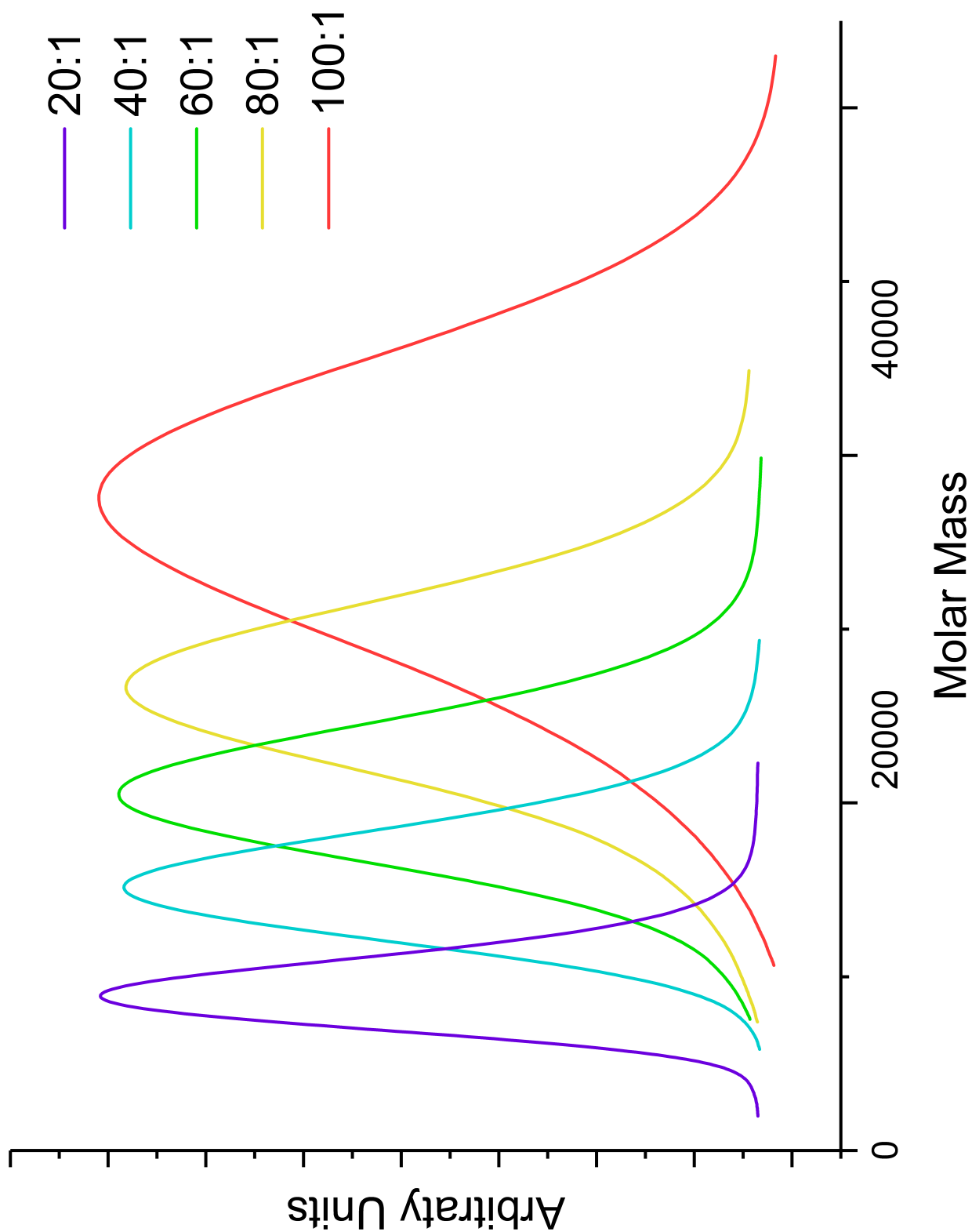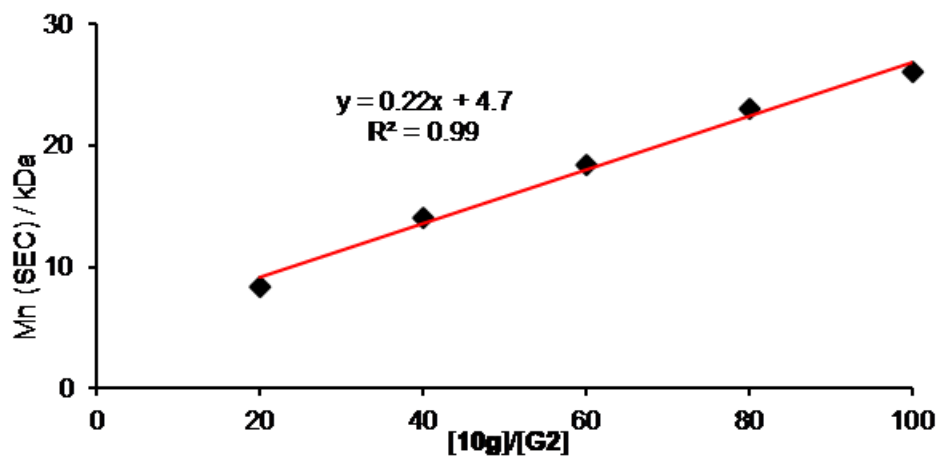Figure 2, right image

216x162mm (120 x 120 DPI)

Mes = 2,4,6-Trimethylphenyl; Cy = cyclohexyl

Figure 3

100x45mm (300 x 300 DPI)

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$$y = 0.22x + 4.7$$
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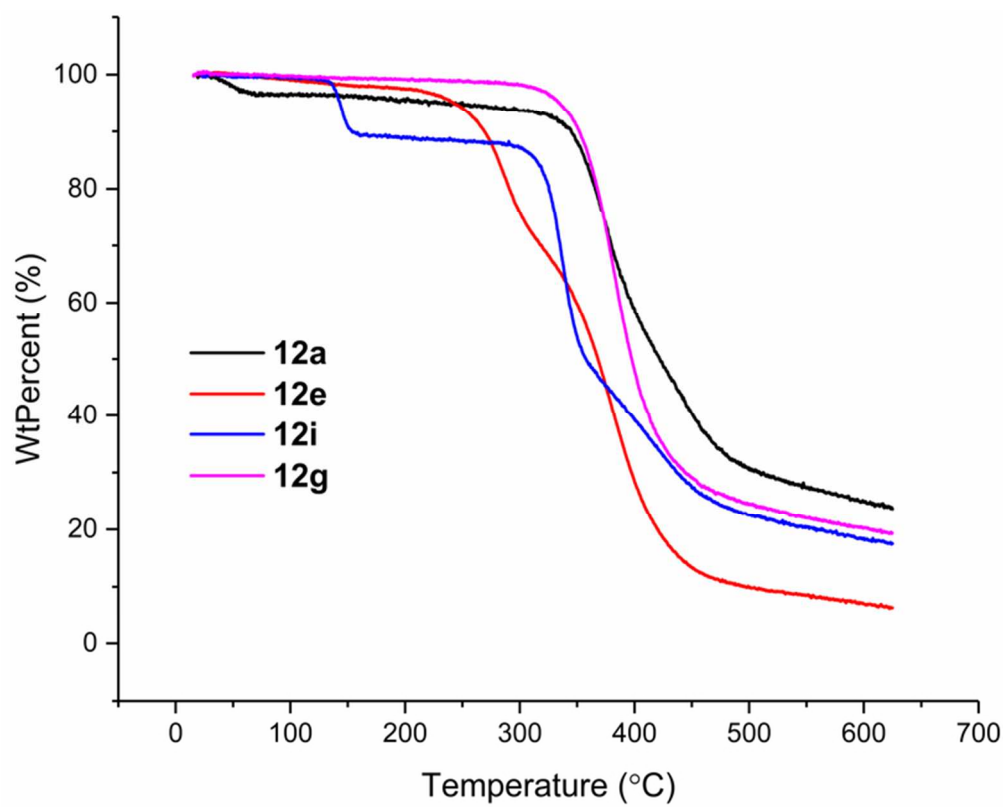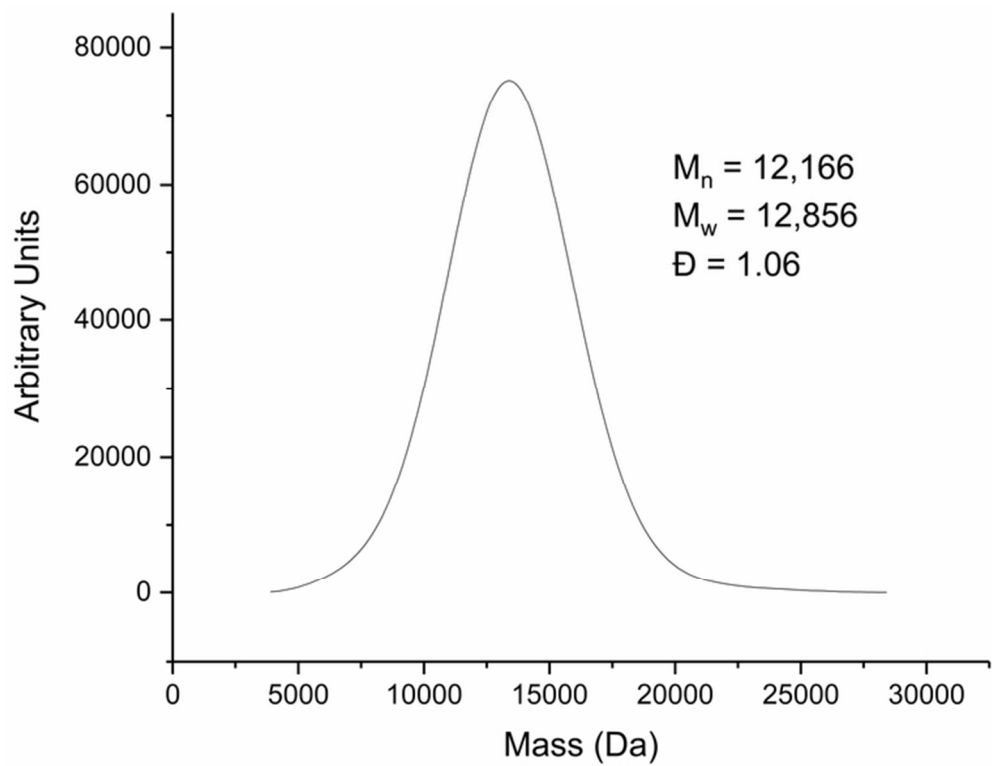

Figure 6

68x55mm (300 x 300 DPI)

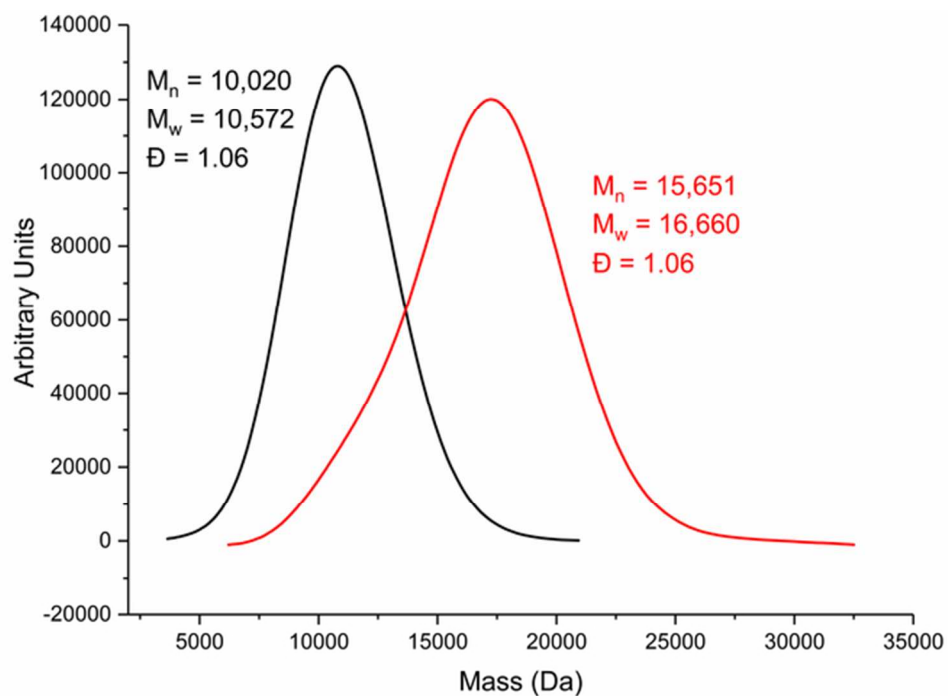Figure 7

65x49mm (300 x 300 DPI)

Figure 8

58x40mm (300 x 300 DPI)

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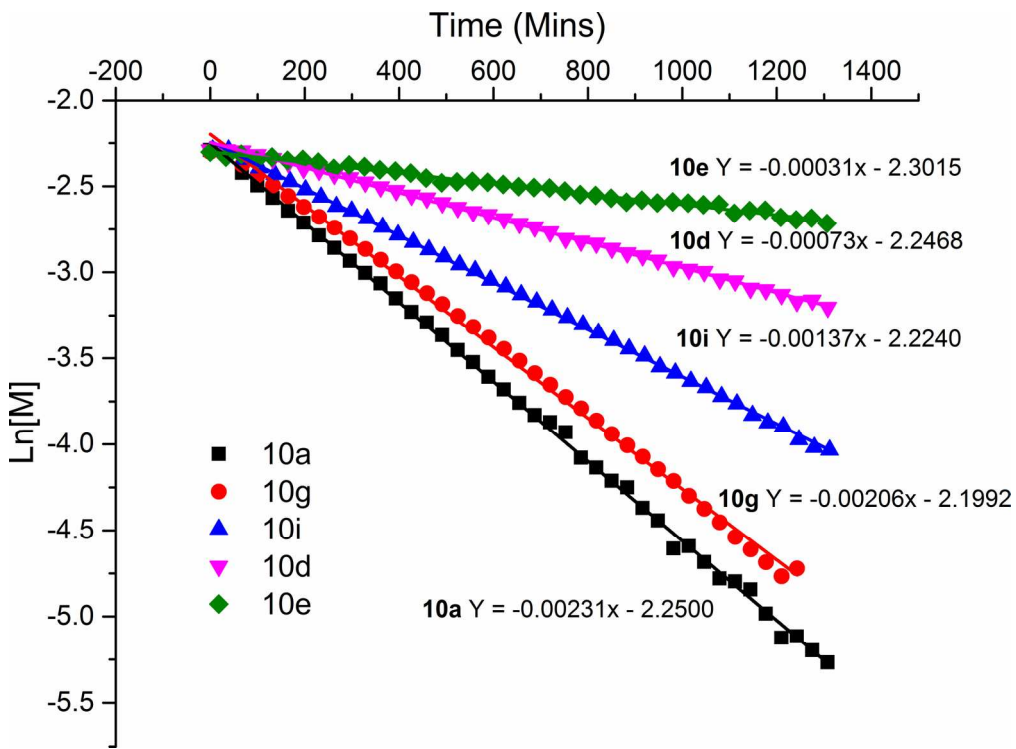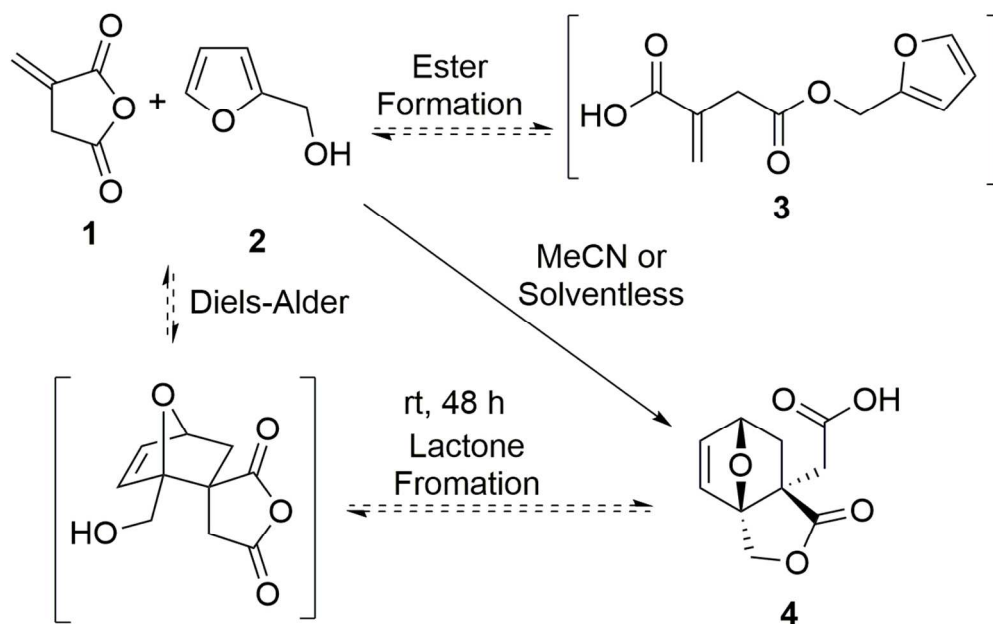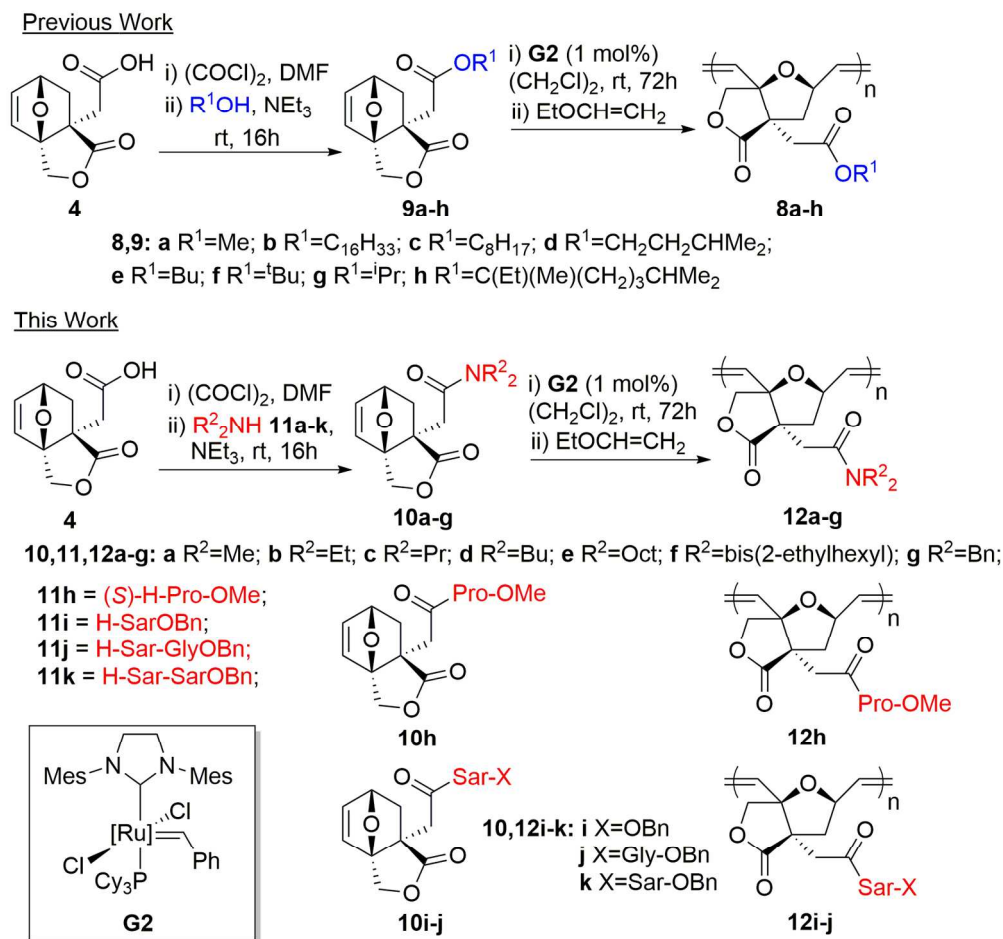41
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Figure 9

170x124mm (300 x 300 DPI)

Scheme 1

108x68mm (300 x 300 DPI)

Previous Work

8,9: a R^1=Me; **b** R^1=$C_{16}H_{33}$; **c** R^1=C_8H_{17}; **d** R^1=$CH_2CH_2CHMe_2$;
e R^1=Bu; **f** R^1=^tBu; **g** R^1=^iPr; **h** R^1=$C(Et)(Me)(CH_2)_3CHMe_2$

This Work

10,11,12a-g: a R^2=Me; **b** R^2=Et; **c** R^2=Pr; **d** R^2=Bu; **e** R^2=Oct; **f** R^2=bis(2-ethylhexyl); **g** R^2=Bn;

11h = (*S*)-H-Pro-OMe;
11i = H-SarOBn;
11j = H-Sar-GlyOBn;
11k = H-Sar-SarOBn;

10,12i-k: i X=OBn
j X=Gly-OBn
k X=Sar-OBn

Scheme 2. ROMP of esters 9a-h and amides 10a-k.

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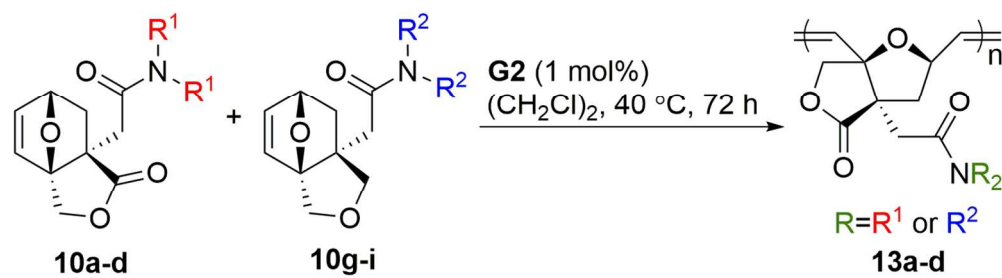
Scheme 3

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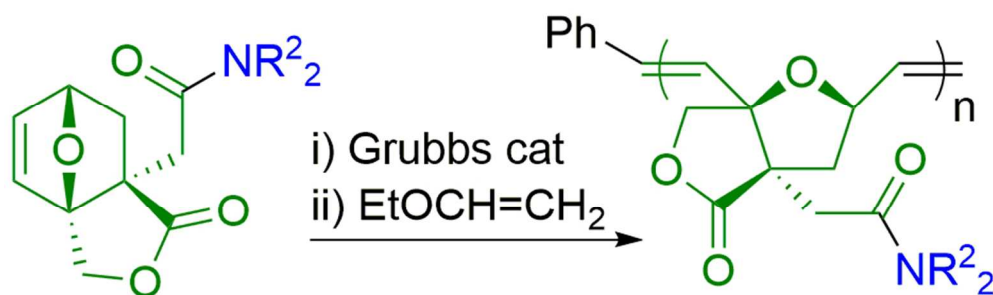51
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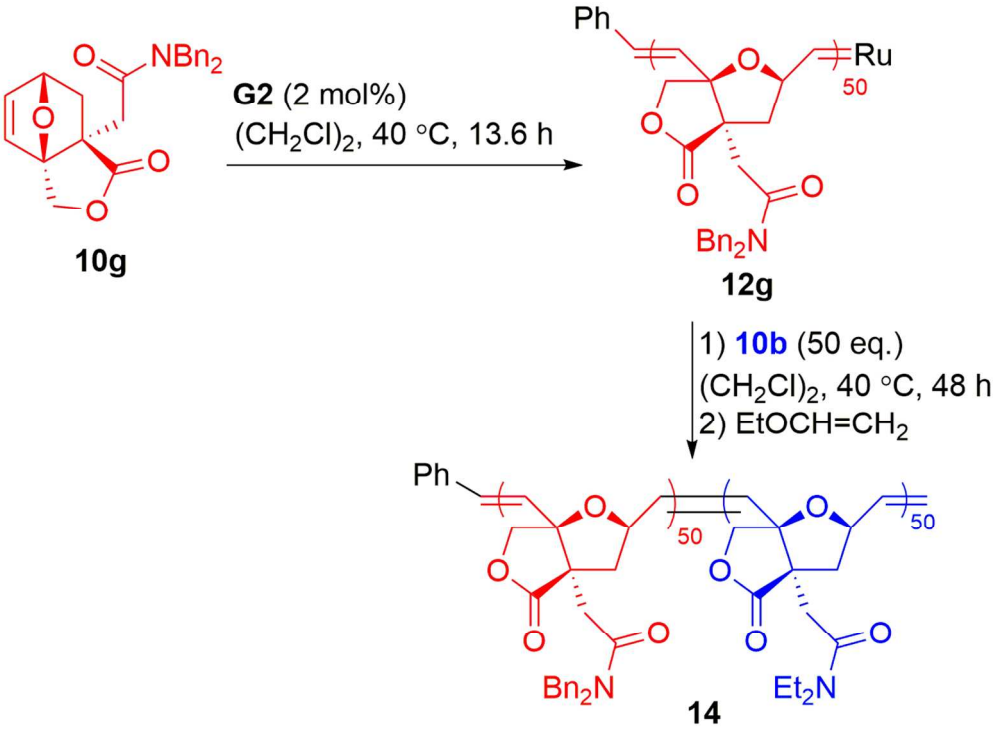
Scheme 4

114x84mm (300 x 300 DPI)

Table of contents graphic

79x24mm (300 x 300 DPI)