

**Original citation:**

Naguib, Mohamed, Schiller, Tara L. and Keddie, Daniel J. (2018) Rapid, regioselective living ring-opening metathesis polymerization of bio-derivable asymmetric tricyclic oxanorbornenes. *Macromolecular Rapid Communications*, 39 (7).  
doi:10.1002/marc.201700794

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**Article Type (Communication)**

**Rapid, regioselective living ring-opening metathesis polymerization of bio-derivable asymmetric tricyclic oxanorbornenes<sup>a</sup>**

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The synthesis of a range of alkyl esters (methyl, *n*-butyl and *n*-decyl) prepared via Steglich esterification of the thermodynamically-controlled *exo,exo* Diels-Alder (DA) adduct of furfuryl alcohol and maleic anhydride is reported. Subsequent ring-opening metathesis polymerization (ROMP) of these bio-derivable tricyclic oxanorbornene analogues delivered polymers with targeted molar mass and low molar mass dispersity. The polymerizations are rapid with complete monomer conversion achieved within 15 minutes. Significantly, the presence of the cyclic lactone at the bridgehead of these monomers leads to polymers with high regio- (>85% head-to-tail) and stereoregularity (>75% *trans*). The resultant polymers display both high thermal stability and high glass transition temperatures. This new class of oxanorbornene monomer, accessed from bio-derivable furfuryl alcohol and maleic anhydride, may be further tailored to incorporate a range of functional moieties. Furthermore, the exceptional properties of the derived polymers indicate potential in range of applications.

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<sup>a</sup> **Supporting Information** ((bold)) is available online from the Wiley Online Library

## 1. Introduction

The molecular microstructure of polymer materials (i.e. sequence and tacticity) is intimately linked to their physicochemical and thermomechanical properties and as such dictates their performance in specific applications. Variations in the synthetic methodology used for the preparation of polymeric materials can lead to stark differences in properties at both the molecular and macroscopic level.<sup>1</sup>

In this context, ring-opening metathesis polymerization (ROMP)<sup>2-3</sup> of strained cyclic olefins offers some unique opportunities with respect to the synthesis of polymers with (pre-)defined microstructural characteristics. For example, control over stereochemistry may be achieved by manipulating the structure of transition-metal catalyst,<sup>4-7</sup> whilst sequence distribution can be tailored via judicious selection of the polymerizing (co)monomers allowing for the synthesis of alternating, random or gradient copolymers.<sup>8-10</sup> Importantly, ROMP enables the preparation of regioregular polymers, bearing defined functional sequences, from appropriately designed monomers. This has been elegantly demonstrated by Parker and Sampson for the preparation of polycyclobutenes,<sup>11</sup> and more recently by Hillmyer in a series of reports detailing the synthesis of regioregular polycyclooctenes.<sup>12-17</sup>

Recently, we have become interested in the synthesis of new monomers derived from bio-based feedstock for the preparation of functional polymeric materials. For this, ROMP is a particularly attractive route as monomers bearing appropriate ring strain to readily undergo polymerization are easily accessible through Diels-Alder (DA) chemistry with renewable furan-based substrates. This has been recently illustrated by Bai *et al.*<sup>18-19</sup> where polymers were prepared, albeit slowly ( $t > 24\text{h}$ ), by the ROMP of tricyclic *endo,exo*-functional DA adducts, derived from furfuryl alcohol and itaconic anhydride. An in depth mechanistic study

of the formation of these tricyclic adducts via tandem Diels-Alder cycloaddition and lactonization has been recently reported by Peher et al.<sup>20</sup>

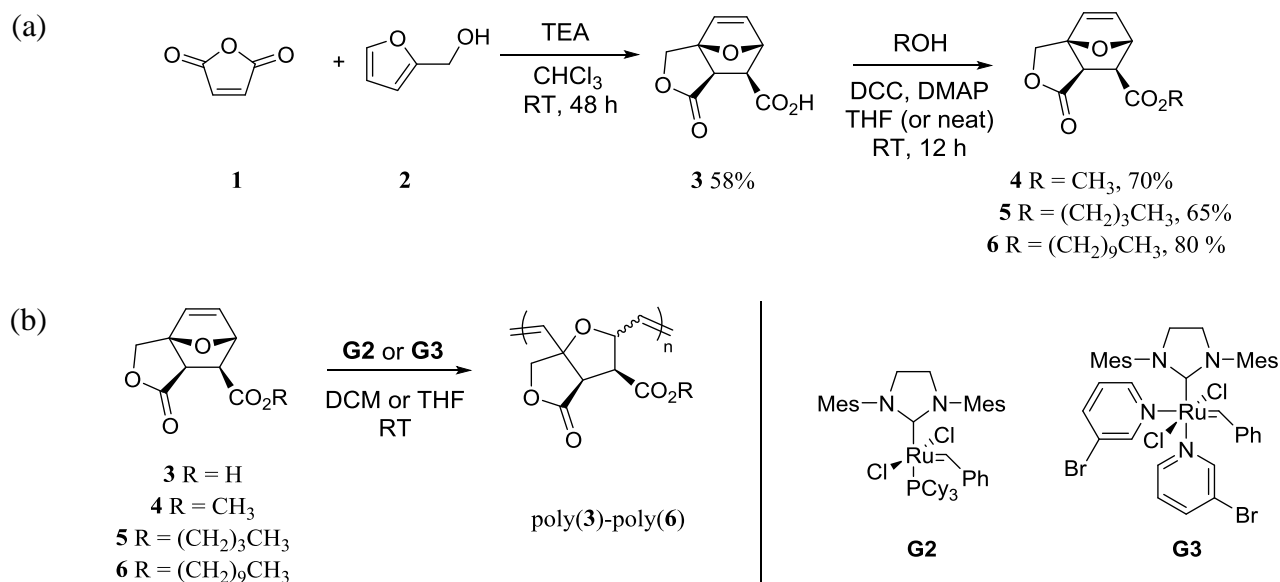
Herein, we report the synthesis and living ROMP of tricyclic oxanorbornene analogues, derived furfuryl alcohol and maleic anhydride, which complements and extends upon the work of Bai *et al.*<sup>18-19</sup> and Hillmyer.<sup>12-17</sup> These new bio-derivable monomers are shown to undergo rapid, regioselective ring-opening during polymerization delivering regioregular polymers of low molar mass dispersity (*D*) and high thermal stability within minutes.

## 2. Results and Discussion

With respect to preparation of bio-derivable monomers amenable to ROMP, the DA adduct of maleic anhydride **1** and furfuryl alcohol **2** is particularly attractive; both starting materials can be obtained renewably from the platform molecule furfural<sup>21-23</sup> and the reaction is known to give the strained tricyclic lactone adduct **3** (over two synthetic steps), by intramolecular DA cyclization following ring-opening of the anhydride by nucleophilic attack of the alcohol group, delivering the product exclusively as the *exo,exo* isomer.<sup>24</sup> We predicted that, in combination, the lack of *endo* substituents and the steric asymmetry on **3** (due to the presence of the bridgehead substituent) may lead to rapid, regioselective ring-opening during ROMP.

We achieved direct synthesis of DA adduct **3** via an improved one-pot process by reaction of **1** and **2**, in the presence of catalytic triethylamine (TEA) in moderate yield (Scheme 1(a)). Conveniently, the pure product **3** crystallizes directly from the reaction mixture. Comparison of the NMR data to previous literature<sup>24</sup> indicates exclusive formation of the desired *exo,exo* isomer.<sup>25-26</sup>

*Scheme 1:* (a) Tricyclic monomer syntheses via Diels-Alder reaction and Steglich esterification (indicating relative stereochemistry) and (b) ring-opening metathesis polymerization of tricyclic lactone carboxylic acid **3** and esters monomers **4-6** (with catalysts **G2** and **G3**)



Although ROMP of the acid-functional **3** provided polymers using both Grubbs 2<sup>nd</sup> (**G2**) (data not shown) and 3<sup>rd</sup> generation (**G3**) (Entry 1, Table 1) catalysts in THF, the resultant polymers had high dispersity ( $D > 2$ ). This lack of control over polymerization is likely due to progressive deactivation of the metathesis catalysts by the free carboxylic acid functionality over the course of the reaction.<sup>27</sup>

Subsequently, the corresponding methyl **4**, *n*-butyl **5** and *n*-decyl **6** esters were prepared to both mask the carboxylic acid functionality and investigate the effect of increased steric bulk of the acyclic ester group during polymerization. Initial attempts at synthesis of the methyl ester **4** via Fischer esterification of the acid **3** were unsuccessful, resulting in an intractable black tar. We postulate this is due polycondensation of furfuryl alcohol formed via retro-DA promoted by acid catalysis and/or high temperature.<sup>28</sup> After changing to Steglich esterification

of **3** with methanol, *n*-butanol or *n*-decanol we could obtain the corresponding esters **4-6** in moderate to high yields (Scheme 1(a)).

*Table 1:* Characterization data for the ROMP synthesized polymers<sup>a)</sup>

Entry	Polymer <sup>b)</sup>	Monomer (M)	Catalyst (I)	[M]/[I]	Conv. %	$M_n$ (g mol <sup>-1</sup> )		$\bar{D}^d$
						(calc.) <sup>c)</sup>	(SEC) <sup>d)</sup>	
1	poly( <b>3</b> ) <sub>100</sub>	<b>3</b>	<b>G3</b>	100:1	99	19400	35700	3.52
2	poly( <b>5</b> ) <sub>100,(G2)</sub>	<b>5</b>	<b>G2</b>	100:1	98	24700	191600 <sup>e</sup>	1.39 <sup>e)</sup>
3	poly( <b>6</b> ) <sub>100,(G2)</sub>	<b>6</b>	<b>G2</b>	100:1	98	32900	382800 <sup>e</sup>	1.26 <sup>e)</sup>
4	poly( <b>5</b> ) <sub>25</sub>	<b>5</b>	<b>G3</b>	25:1	99	6200	21500	1.11
5	poly( <b>5</b> ) <sub>50</sub>	<b>5</b>	<b>G3</b>	50:1	99	12500	42900	1.11
6	poly( <b>5</b> ) <sub>100</sub>	<b>5</b>	<b>G3</b>	100:1	98	24700	85600	1.12
7	poly( <b>5</b> ) <sub>200</sub>	<b>5</b>	<b>G3</b>	200:1	98	49600	231600	1.15
8	poly( <b>6</b> ) <sub>25</sub>	<b>6</b>	<b>G3</b>	25:1	99	8300	26800	1.08
9	poly( <b>6</b> ) <sub>50</sub>	<b>6</b>	<b>G3</b>	50:1	98	16500	62200	1.14
10	poly( <b>6</b> ) <sub>100</sub>	<b>6</b>	<b>G3</b>	100:1	98	32900	104700	1.08
11	poly( <b>6</b> ) <sub>200</sub>	<b>6</b>	<b>G3</b>	200:1	98	65900	248800	1.19
12	poly(( <b>5</b> ) <sub>50</sub> - <i>bl</i> -( <b>7</b> ) <sub>50</sub> )	<b>5</b> then <b>7</b>	<b>G3</b>	50:50:1	99	23400	100200	1.23
13	poly(( <b>6</b> ) <sub>50</sub> - <i>bl</i> -( <b>7</b> ) <sub>50</sub> )	<b>6</b> then <b>7</b>	<b>G3</b>	50:50:1	98	27300	99100	1.18

<sup>a)</sup>Polymerization was performed in DCM (except THF was used for Entry 1) at room temperature, <sup>b)</sup>subscript indicates the targeted degree of polymerization (DP) of the monomer in parentheses, <sup>c)</sup> $M_n(\text{calc.}) = [M]_0/[I]_0 \times M_r \times \text{conv. \%}$ , <sup>d)</sup>SEC THF eluent,  $T = 40^\circ\text{C}$  (data reported in polystyrene equivalents), <sup>e)</sup>SEC traces show bimodal distributions (the data of major peak is reported).

ROMP of the methyl ester **4** was attempted with **G3** in both THF and chloroform as solvent. The polymethyl ester was found to precipitate from the reaction mixture after ~10 min in both solvents (data not shown), which we attribute to lack of solubility of the polymer produced.<sup>29</sup> Conversely, ROMP of both the *n*-butyl **5** and *n*-decyl **6** esters with either **G2** or **G3** remained homogeneous, proceeding rapidly with almost complete monomer conversion (>98 %) achieved within ~15 minutes (see Scheme 1(b)). These reactions provide soluble polymers of low molar mass dispersity (see Table 1). We ascribe the successful ROMP of **5** and **6** to increased solubility of the ROMP-derived polymers due to the longer alkyl chains. The cyclic lactone at the bridgehead appears to be important for rapid polymerization kinetics; acyclic bridgehead substituents on oxanorbornenes have previously been shown to hinder homopolymerization and induce alternation in copolymerization with cyclooctene.<sup>9</sup> The rapid polymerization of **5** and **6** is exemplified when using the slow initiating **G2** catalyst; polymers with very high molar mass and increased *D* were obtained (see Entries 2 & 3, Table 1). In contrast, polymers prepared with the fast initiating **G3** had very low *D* and molar masses closer to the calculated  $M_{n(\text{calc.})}$ .<sup>30</sup>

The polymers obtained by ROMP of **5** or **6** display high *trans*-stereoselectivity (>75%) as evident from analysis of the vinylic region of the <sup>1</sup>H NMR spectra (e.g. poly(**5**)<sub>100</sub>: ~73% *trans*<sub>HT</sub> + ~8% *trans*<sub>HH</sub>, see Figure 1a; poly(**6**)<sub>100</sub>: ~68% *trans*<sub>HT</sub> + ~9% *trans*<sub>HH</sub> see Figure 21S in the supporting information). Inspection of the vinylic region in the <sup>13</sup>C NMR spectra of poly(**5**) and poly(**6**), clearly showing only two appreciable <sup>13</sup>C resonances in each case, indicates high regioregularity (>85% head-to-tail (HT)) (e.g. poly(**5**)<sub>100</sub>: ~73% *trans*<sub>HT</sub> + ~14% *cis*<sub>HT</sub>, see Figure 1a and b; poly(**6**)<sub>100</sub>: ~68% *trans*<sub>HT</sub> + ~17% *cis*<sub>HT</sub>, see S21 and 22S for poly(**6**) in the supporting information). This is further confirmed by the presence of a key C-H correlation in the HMBC NMR spectra between the bridgehead quaternary carbons and

vinylc protons from the adjacent monomer units (see Figure 1c for poly(**5**)<sub>100</sub> and 25S for poly(**6**)<sub>100</sub>). This, to the best of our knowledge, is the first example of regioselective ROMP of asymmetric (oxa)norbornenes. We postulate steric repulsion between the lactone substituent at the bridgehead of the monomer and the *N*-heterocyclic carbene (NHC) ligand of the metathesis catalyst (and the propagating chain) leads to a preferred method of monomer approach during polymerization.

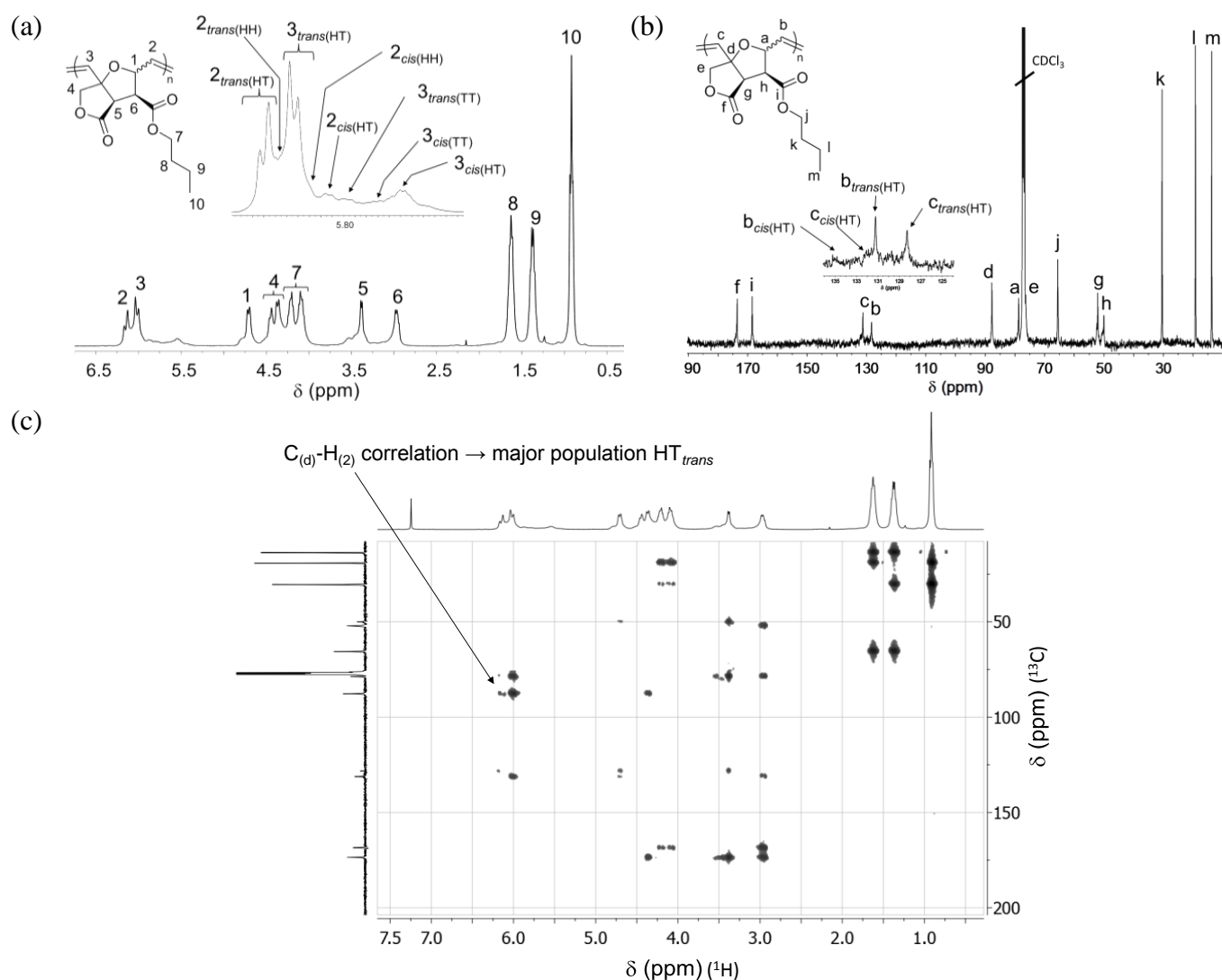


Figure 1: (a) <sup>1</sup>H, (b) <sup>13</sup>C and (c) HMBC NMR spectra of polybutyl ester ROMP polymer (poly(**5**)<sub>100</sub>). (Stereo- and regiochemistry assigned via COSY, HSQC and HMBC experiments.)



Note that different length alkyl substituents on the acyclic ester, i.e. butyl vs decyl, have a limited effect over resultant polymeric microstructure. This adds further support to this hypothesis. More in depth investigation into the effects of monomer and/or catalyst sterics upon polymer microstructure is currently ongoing within our laboratories.

To investigate the “livingness” of the system during ROMP of **5** and **6**, the monomer to catalyst ratio ( $[M]/[I]$ ) was varied between 25:1 and 200:1. A linear relationship between  $[M]/[I]$  and number-average molar mass ( $M_n$ ) was observed, with reactions giving polymers of low dispersity ( $\bar{D} < 1.2$ ) in all cases, illustrating good control over the polymerization process (see Table 1 and Figure S32 & S33). Note that the molar masses obtained from SEC are higher than predicted theoretically, likely due to the difference in the hydrodynamic volume of the ROMP polymers in solution compared to that of polystyrene standards.<sup>30</sup>

To further investigate the ROMP of alkyl esters **5** and **6**, block copolymers were synthesized by block extension of their respective polymers with *N*-butyl oxanorbornenedicarboximide (NBOD) **7**<sup>31</sup> (see Figure S34 in the supporting information). In each case a clear shift to a higher molar mass upon the addition of NBOD was observed by SEC analysis, delivering block copolymers of low  $\bar{D}$ . The molar mass distribution of the diblock copolymers were narrow indicating the successful block extension of poly(**5**) or poly(**6**) with **7** via sequential ROMP (poly((**5**)<sub>50</sub>-*bl*-(**7**)<sub>50</sub>):  $\bar{D}$ = 1.23; poly((**6**)<sub>50</sub>-*bl*-(**7**)<sub>50</sub>):  $\bar{D}$ = 1.18, see Table 1 Entries 12 & 13 respectively).

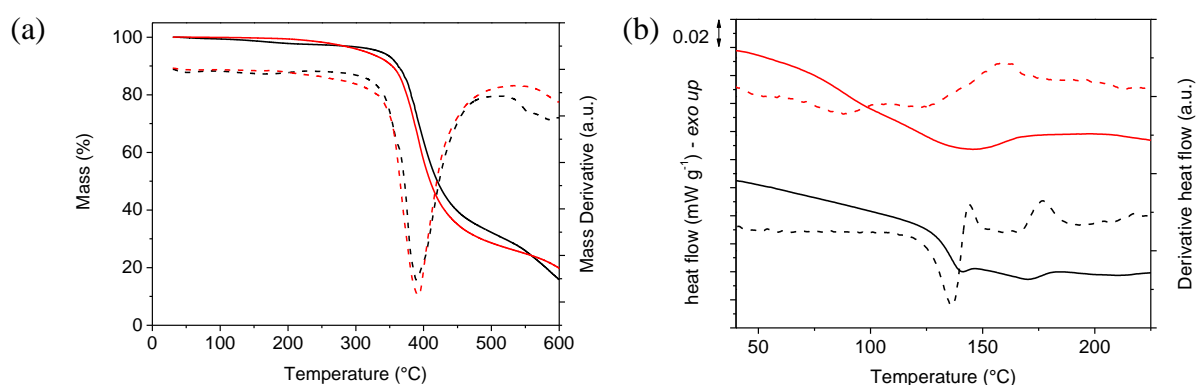


Figure 2: (a) TGA (solid lines) and DTA curves (dashed lines), and (b) DSC traces (solid lines) and smoothed derivatives (dashed lines) for the polybutyl ester (poly(**5**)<sub>50</sub>) (black lines) and the polydecyl ester (poly(**6**)<sub>50</sub>) (red lines). DSC traces offset for clarity.

The homopolymers derived from the esters **5** and **6** are thermally stable to high temperature as indicated by TGA (the  $T_{d,onset} \approx 350$  °C, see Figure 2a)). The thermograms reveal slight differences in hydrophilicity between the two polymers, with the polybutyl ester (poly(**5**)<sub>50</sub>) displaying a slight mass loss corresponding to absorbed moisture ( $\approx 2.5\%$ ). DSC analysis (Figure 2b) indicates that both polymers possess high  $T_g$  values, with the length of alkyl chain having an discernible effect ( $T_g = 136$  °C for polybutyl ester, poly(**5**)<sub>50</sub>, and  $88$  °C for polydecyl ester, poly(**6**)<sub>50</sub>). The longer alkyl chain in poly(**6**) is likely to behave as internal plasticizer, resulting in the lower  $T_g$  observed. A crystallization peak also appears to be present for both polymers; the crystallization behaviour induced by high regularities of these polymers will be the subject of future investigation.

## 4. Conclusions

We have described the optimized synthesis of a new monomeric platform for the synthesis of bio-derivable polymers via ROMP. When using **G3** as the metathesis catalyst, polymers of low  $\bar{D}$  are obtained within minutes which display high *trans*-stereoselectivity (>75%) and HT regioregularity (>85%). Livingness of the system is displayed by a linear correlation between catalyst loading and experimental  $M_n$ . The resulting ROMP synthesized polymers possess relatively high  $T_g$  values and exceptional thermal stability. These combined properties indicate the potential of these polymers in a range of applications. Further development of polymer materials derived from this monomeric platform is currently ongoing within our laboratories.

## Supporting Information

Supporting Information is available from the Wiley Online Library. This includes materials, characterization methods, monomer and polymer synthesis, and characterization data.

## Acknowledgements

M. N. would like to thank the cultural affairs & missions sector of Egypt for the financial support. D.J.K acknowledges the Royal Society of Chemistry and the Faculty of Science and Engineering at the University of Wolverhampton for funding.

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29. We postulate a high level of crystallinity arising from regioregular ROMP of the methyl ester (as per the butyl and decyl esters) leads to low solubility of the resulting polymer resulting in precipitation during the polymerization
30. A discrepancy between  $M_n(\text{calc.})$  and  $M_n(\text{SEC})$  is present within the data due to the use of conventional calibration curve using low dispersity polystyrene standards to obtain the  $M_n(\text{SEC})$  value.
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**Ring-opening metathesis polymerization is exploited to prepare low dispersity polymers of high regioregularity and thermal stability from bio-derivable tricyclic oxanorbornenes.** This new monomeric platform is readily accessible via esterification following Diels-Alder lactonization of furfuryl alcohol and maleic anhydride. Steric repulsion between the metathesis catalyst NHC and the bridgehead substituent leads to polymers with head-to-tail regiochemistry in excess of 85%.

Mohamed Naguib\*, Tara L. Schiller, and Daniel J. Keddie\*

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