

Acyclic diene metathesis (ADMET) polymerization of allyl undec-10-enoate and some related esters

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Abstract

When several diallyl esters were subjected to ADMET using Grubbs “first generation” catalyst only oligomerization occurred (DPs < 7), but with allyl hex-5-enoate the product had a DP of 14, and with allyl undec-10-enoate the products usually had DPs in the range 41–79. It is suggested that with the diallyl esters an intermediate is formed in which the ester carbonyl chelates onto the metal centre and that this is sufficiently stable to suppress polymerization. One possible explanation for the successful polymerization of allyl undec-10-enoate is that it is achieved *indirectly* via a ring-closing metathesis (RCM) to give a macrocycle that then reacts further by an entropically driven ring-opening polymerization (ED-ROMP) to give the final polymer. A cyclo-depolymerization (CDP) involving the metathesis of *substituted* allyl ester moieties in a polymer backbone and ED-ROMPs involving the metathesis of *substituted* allyl ester moieties in macrocycles catalyzed by Grubbs’ “first generation” catalyst and/or the “second generation” catalyst were also successful. © 2006 Elsevier B.V. All rights reserved.

Keywords: ADMET; ED-ROMP; Metathesis of allyl esters

1. Introduction

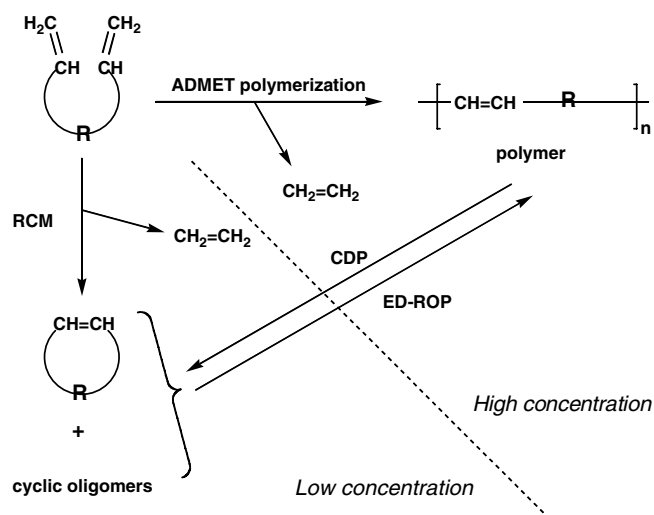
Condensation polymers and the corresponding monomers and macrocycles can generally be interconverted by a series of closely related reactions, where the nature of the major reaction product(s) depends greatly on the concentrations of the reactants [1–3].

The reactions are summarized in **Scheme 1** for olefin-containing reactants that are interconverted via olefin metathesis [4–6]. In connection with our interest in the potential applications of such reactions [2,7], in particular the preparation of combinatorial libraries of either macrocycles [8] and/or polymers [9], we sought to polymerize a range of ω -alkenyl undec-10-enoates by acyclic diene metathesis (ADMET) [10] using the commercially available Grubbs “first generation” catalyst **1**. Our aim was to determine the minimum number of methylene groups that can be present in the *O*-alkenyl group for the polymerization

to be successful using this catalyst. We wished to use catalyst **1** rather than the Grubbs “second generation” catalyst **2** because the latter can cause carbon–carbon double bond migration [11,12] and this could clearly cause problems in combinatorial studies.

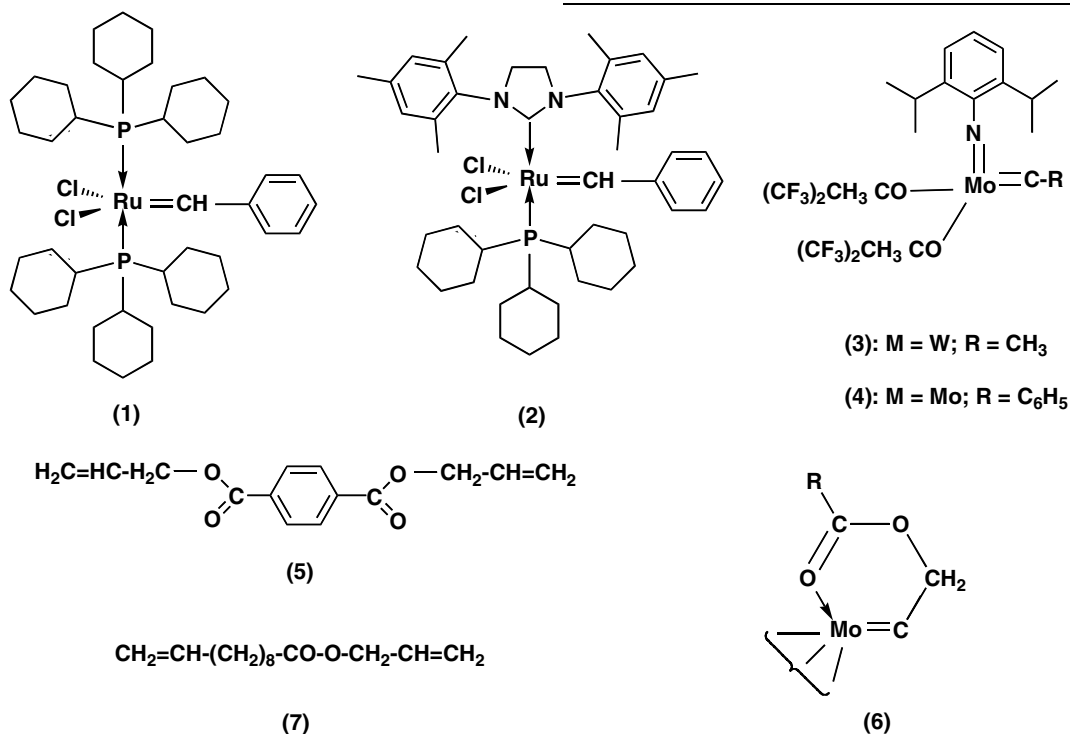
Various ω -alkenyl esters have been polymerized successfully by ADMET before using Schrock’s catalysts **3** or **4** [13,14], but attempts to polymerize allyl esters have met with little success [14]. For example, diallyl terephthalate (**5**) did not polymerize when treated with Schrock’s catalyst **3** [14]. The failure of allyl esters to polymerize has been attributed to a “negative neighbouring group effect” in which the ester carbonyl group binds to the metal centre as part of a six-membered ring, see formula **6**, and in so doing deactivates the catalyst [14–16]. Success at polymerizing carbonate-containing α,ω -dienes using a molybdenum-based catalyst depends similarly on the number of methylene spacers between the carbonyl groups and the vinyl groups [17]. So too does the polymerization of ether-containing α,ω -dienes using a tungsten-based catalyst even though the ether oxygen atom is a weaker Lewis acid than

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Scheme 1. Scheme showing relationship of monomer, polymer and cyclic oligomers interconverted by olefin metathesis. ADMET = acyclic diene metathesis; RCM = ring-closing metathesis; CDP = cyclo-depolymerization; ED-ROP = entropically driven ring-opening polymerization.

an ester carbonyl oxygen atom [18]. A macrocycle containing an olefinic moiety flanked by two $-\text{CH}_2\text{O}-$ has however been found to undergo ED-ROMP successfully [19].



It should be noted that using metathesis to form olefinic linkages between the repeat units of a polymer is much more demanding than, for example, a RCM reaction. The latter might be deemed a success if the yield is 75%, but a similar efficiency in an ADMET polymerization

would give a product with an DP of only 4, i.e. only very small oligomers [20]. To obtain a polymer with a DP of, say, 50 will require the formation of 49 linkages with an average yield for each one of 98% [20]. Thus, the fact that catalyst **1** has been used successfully, sometimes with only modest yields however, to metathesize, for example, allyl esters [21–25], allyl ethers [23,24,26,27] and allyl alcohol [11], often in cross metathesis [21,22] or RCM reactions [24–26] and for end-capping polymers [21,22], does not necessarily mean analogous reactions can be used successfully for polymer synthesis.

In this paper we report that several ω -alkenyl undec-10-enoates undergo ADMET polymerization successfully using Grubbs' "first generation" catalyst **1** including, surprisingly, allyl undec-10-enoate (**7**). Several other allyl esters failed to polymerize but they did oligomerize. However, *substituted* allyl ester moieties in polymers and in macrocycles react successfully using catalyst **1** and/or Grubbs' "second generation" catalyst **2**.

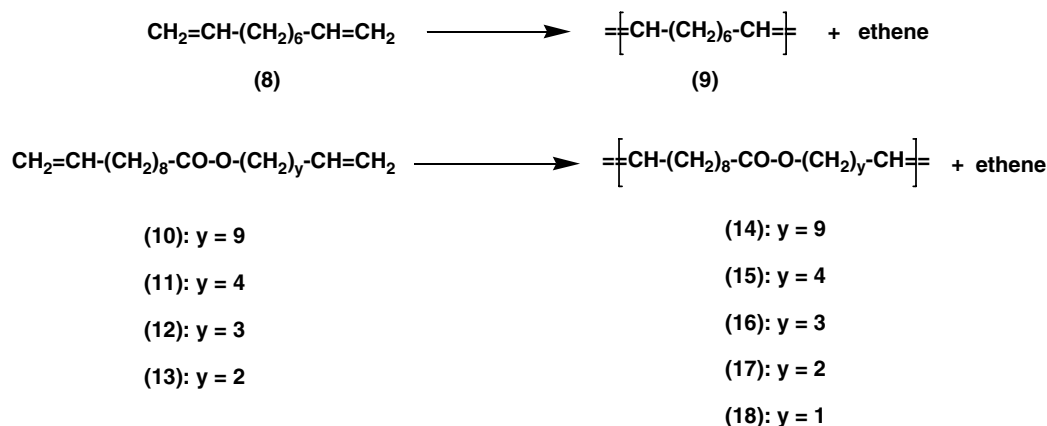
2. Results and discussion

Initially, to establish our polymerization procedure, we polymerized deca-1,9-diene (**8**) [28,29]. The *neat* diene **8** was first stirred with 1 mol% of catalyst **1** at 20 °C under an atmosphere of dry argon. The mixture effervesced vigor-

ously as ethene was evolved. After 18 h, to remove any remaining ethene, the solid product was dissolved in chloroform and the solution evaporated to dryness. The residue was then dissolved in dichloromethane and retreated at 20 °C with fresh catalyst **1** for 18 h. During this period most

of the dichloromethane evaporated off. The solution polymerization was then repeated again using fresh catalyst. Finally the remaining solvent was replaced by chloroform and the mixture precipitated into methanol. This gave polyoctenamer (**9**) with, by GPC relative to polystyrene standards, M_n 12000 and M_w 24100. The number average molecular weight corresponds to an average degree of polymerization (DP) of 109. The FT-IR and ^1H NMR spectra were satisfactory. These results are summarized in Table 1, entry 1:

to give, respectively, polymers **14–18**. In all cases the *E*–*Z*-isomer ratios were approximately 80%:20%. In view of the earlier ADMET results with catalysts **3** and **4** [13,14,17,18], it was not surprising that the experiments with monomers **10–13** were successful, but *the success with allyl undec-10-enoate (7) was very surprising*. Accordingly the polymerization of **7** was repeated several times. The M_n values of polymer **18** were usually in the range 8000–17000, corresponding to DPs of 41–87, with polydispersities close to 2.0.



Using the same general polymerization procedure attempts were made to polymerize the series of esters **10–13** and **7** in which the number of methylene spacers between the ester group and the vinyl group decreases. The results are summarized in Table 1, entries 2–6. It is evident that all the monomers underwent ADMET

To see if the polymerization of allyl esters using catalyst **1** was general, attempts were made to polymerize diallyl terephthalate (**5**), diallyl isophthalate (**19**) and diallyl adipate (**20**). All these polymerizations were *unsuccessful* and only oligomers were formed with DPs < 7: see Table 1, entries 7–9. In several cases ^1H NMR spectra confirmed

Table 1
ADMET reactions using Grubbs “first generation” catalyst **1**^a

Entry	Monomer	Polymer	Reaction time (h) ^b	Yield (%) ^c	Molecular weights ^d		Degree of polymerization ^e	MALDI-MS data ^f
					M_n	M_w		
1	8	9	54	74	12.0	24.1	109	–
2	10	14	54	83	13.0	39.8	42 ^g	–
3	11	15	54	86	13.7	39.0	57 ^g	–
4	12	16	54	61	18.2	39.1	81 ^g	–
5	13	17	54	71	9.0	18.7	45 ^g	–
6	7	18	54	91	14.6	33.0	79	–
7	5	–	72	93	0.8	1.0	4 ^h	L2–L8
8	19	–	72	92	0.6	0.7	3 ^h	–
9	20	–	54	94	1.3	8.3	7 ^h	C2–C4
10	8+20 ⁱ	–	96	87	1.2	3.9	8	^j
11	21	22	54	54	1.6	2.8	14	–

^a See Section 4 for full details of a typical polymerization.

^b The sum of time for the three stages of the polymerization.

^c After precipitation.

^d Kilograms per mole. Determined by gel permeation chromatography relative to polystyrene standards.

^e Calculated from M_n .

^f Major mass peaks were observed due to the species indicated.

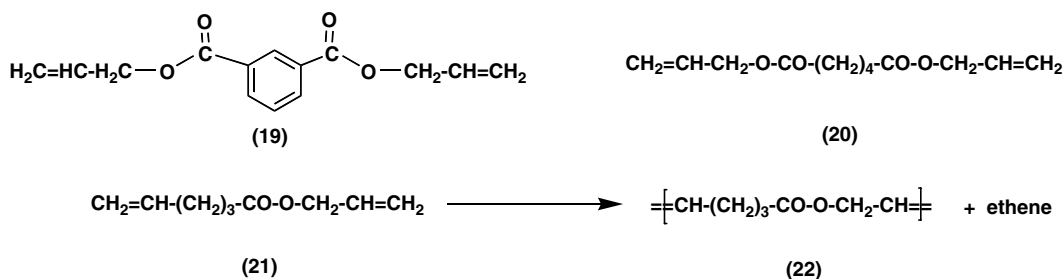
^g By ^1H NMR spectroscopy (see Ref. [33] for an example) the DPs of the polymers were as follows: **14**, 60; **15**, 64; **16**, 80; **17**, 46; **18**, 82.

^h By ^1H NMR spectroscopy the DPs of the oligomers from the various monomers were as follows: **4**, 4; **19**, 3; **20**, 6.

ⁱ 50 mol% of each monomer was used.

^j No mass peaks due to oligodecadienes were observed but mass peaks were observed due to linear dimers, trimers and tetramer of oligo(diallyl adipate) and co-oligomers up to the heptamer.

the GPC results: see footnotes in Table 1. Thus, the same chelation effect noted above for allyl esters with catalyst **3** also seems to operate with catalyst **1** and the results with allyl ester **7** are exceptional. The success with monomer **7**, which contains a readily metathesized vinyl group as well as the allyl group, suggested that deca-1,9-diene (**8**) might copolymerize with diallyl adipate (**20**), but again only oligomers and co-oligomers with DPs < 8 were obtained: see entry 10. Apparently in this case the allyl ester must bind to the catalyst so strongly and so rapidly that the deca-1,9-diene (**8**) is even prevented from homopolymerizing. Thus, it appears that for polymerization of allyl esters to occur *the readily polymerized vinyl group (i.e. the one in the undecenoate moiety) needs to be in the same molecule as the allyl ester*. This prompted an attempt to polymerize allyl hex-5-enoate (**21**). ADMET of this monomer was, however, only moderately successful, see entry 11, with the polymer **22** having a DP of 14, i.e. higher than the allyl esters **5**, **19** and **20**, but much lower than ester **7**. Thus, the order of the ease of reaction is allyl undec-10-enoate (**6**) > allyl hex-5-enoate (**21**) > diallyl terephthalate (**5**). It is apparent that isomerization of the allyl ester group to a vinyl ester group, if it occurs at all, is not a major problem here:



In an attempt to throw further light on the ADMET of allyl undec-10-enoate (**7**), the polymer **18** formed was analyzed by ^{13}C NMR spectroscopy. This allows the proportions of head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) linkages to be determined. It should be noted that since a polymer was obtained, the proportions of HH and TT linkages must be equal. Assuming the undec-10-enyl unit is the head group and the allyl unit the tail group, if the head groups are much more reactive an HH link would be formed first, followed later by TT linkages and polymer **18** would contain only HH and TT linkages. In view of the failure of the various diallyl esters to polymerize this does not appear to be a reasonable polymerization mode. If the H and T monomer units were equally reactive the repeat units would be linked statistically. In this case the expected proportions of HT:HH:TT linkages are 50:25:25. In practice, however, it was found that the percentages of HT linkages (see Table 2, entry 5) were 66–75%. Thus the percentage of HT linkages was significantly higher than statistical. The actual percentage formed by the initial ADMET

may actually have been higher still because secondary metathesis, which is relatively slow because 1,2-disubstituted olefinic linkages are involved [5,6,30], will tend to shift the initial proportions towards the statistical proportions.

The proportions of HT units were also determined for polymers **15–17**. The results, summarized in Table 2 entries 2–4, indicate that the proportions of HT linkages is, within experimental error, the statistical proportion, i.e. 50%, when the ester and vinyl group are separated by only four methylene groups and even when there are only two methylene groups it is still very close, 53%, to being statistical.

It is not clear why allyl undec-10-enoate (**7**) can be polymerized when other allyl esters undergo ADMET so poorly. An intriguing *possibility* that explains many of the above observations is the following:

- (i) The allyl group of allyl undec-10-enoate (**7**) reacts rapidly with the catalyst to give an intermediate analogous to that shown in formula **6**.
- (ii) This then reacts further by cross metathesis with the vinyl group of the undec-10-enoate moiety *in the same molecule*, i.e. by ring-closing metathesis

(RCM), to give the unsaturated cyclic ester **23**. This has 13 ring atoms and hence has little or no strain [31]. Clearly in this macrocycle all the olefinic moieties are in the HT arrangement. Note that in the case of allyl hex-5-enoate (**21**) the corresponding cyclic intermediate is an eight-membered ring, i.e. a *strained* medium-sized ring [31].

- (iii) Finally, the cyclics **23**, under the high concentration reaction conditions, undergo entropically driven ring-opening polymerization (ED-ROMP) to give the polymer **18** [2,4].

A possible alternative to (i) and (ii) is that the olefinic moiety in the undec-10-enoate group of **7** reacts with the catalyst first and that this then causes the allyl group to undergo RCM to give **23**.

To summarize, there is the possibility that instead on monomer **7** affording polymer **18** *directly* by ADMET, monomer **7** undergoes RCM to give macrocycle **23** which then undergoes ED-ROMP so giving polymer **18** *indirectly*: see Scheme 1.

Table 2
Percentages of head-to-tail, head-to-head and tail–tail linkages in polymers **15–18**

Entry	Polymer		Signals for in-chain olefinic C-atoms ^a				Percentage head-to-tail linkages
			H–T		H–H	T–T	
			H	T			
1	14	<i>E</i> -isomer	(129.99) ^b	(129.99) ^b	(129.99) ^b	(129.99) ^b	–
		<i>Z</i> -isomer	(129.52)	(129.52)	(129.52)	(129.52)	–
2	15	<i>E</i> -isomer	130.65 ^c	129.22 ^c	129.96 ^c	129.89 ^c	50.0
		<i>Z</i> -isomer	130.13	128.74	129.50	129.37	
3	16	<i>E</i> -isomer	131.02 ^c	128.30 ^c	129.87 ^c	(129.45) ^c	51.0
		<i>Z</i> -isomer	130.57	127.79	(129.45)	128.97	
4	17	<i>E</i> -isomer	133.01 ^d	124.75 ^d	129.91 ^c	127.91 ^c	52.8
		<i>Z</i> -isomer	132.39	124.03	129.44	127.09	
5	18	<i>E</i> -isomer	136.04 ^b	123.57 ^b	129.96 ^c	(127.77) ^f	66.0 ^g
		<i>Z</i> -isomer	134.90	123.14	129.49	(127.77)	

^a The set of eight signals for the in-chain olefinic C-atoms were assigned on the basis of the following. Parenthesis indicates significant overlap of signals and an accurate shift value not determined.

- (i) Each C=C can exist as both *E*- and *Z*-isomers. The signal for the *Z*-isomer will usually appear at a shift value about 0.5 ppm lower than the *E*-isomer (see Ref. [33]). Usually the latter will be the main isomer present.
- (ii) The intensities of the H–H and T–T signals will be equal. So too will the intensities of the H–T and T–H signals.
- (iii) Within experimental error all the H–H signals should appear at the same shifts since in every case the CH=CH is flanked by (CH₂)₈ chains.

^b *E*:*Z* ratio 90:10.

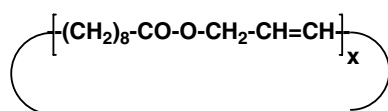
^c *E*:*Z* ratio 80:20.

^d *E*:*Z* ratio 75:25.

^e *E*:*Z* ratio 70:30.

^f *E*:*Z* ratio could not be determined.

^g In other samples of polymer **18** the percentage of H–T linkages was 69.1 and 74.8.



(23): $x = 1$

(24): $x > 1$

Against this general scheme it is reported that the RCM of allyl dodec-11-enoate using catalyst **1** is very difficult though the corresponding *N*-*t*-Boc amide undergoes RCM in 20% yield [32]. Nevertheless, in an attempt to seek support for macrocycle **23** being an intermediate, the polymer **18** was cyclo-depolymerized (CDP) by treating a dilute solution with Grubbs “second generation” catalyst **2** at 40 °C for 6 h [4]. This gave a mixture of cyclics **23** and **24** in 70% yield. The main component under these equilibration conditions was the cyclic monomer **23** (42% by weight). A similar CDP could be achieved using catalyst **1** but the reaction was much slower and after 5 days at 40 °C the yield was only 43% [4]. Even so, these results indicate that the *substituted* allyl ester moieties in polymer **18** undergoes olefin metathesis with both catalysts **2** and **1**, even if rather slowly with the latter.

When the *neat* mixture of macrocycles from the first CDP was treated with catalyst **1** at 40 °C for 36 h an ED-ROMP occurred to give the polymer **18** in 80% yield,

with M_n 15 300 and M_w 32 400, and 70% of the linkages HT. A similar ED-ROMP using catalyst **2** at 40 °C for 12 h gave polymer **18** in 67% yield with M_n 12 100 and M_w 23 450, and 69% of the linkages HT. These results also indicate that *substituted* allyl ester moieties undergo metathesis.

It is not clear why the *substituted* allyl ester moieties undergo metathesis, but it may be that the alkyl substituent at the γ -position of the allyl ester moiety for steric reasons discourages the formation of chelates analogous to **6**. In the case of cyclic **23** it may be that the restricted conformations of the 13-membered ring prevent both the olefinic group and carbonyl oxygen binding to the metal centre at the same time.

3. Conclusions

When several diallyl esters were subjected to ADMET using Grubbs “first generation” catalyst **1** only oligomerization occurred (DPs < 7), but with allyl hex-5-enoate (**21**) the product had a DP of 14, and with allyl undec-10-enoate (**7**) products **18** had DPs up to 87. We suggest that with the diallyl esters an intermediate analogous to **6** is formed and that this is sufficiently stable to suppress polymerization. A similar effect has also been observed when α,ω -divinyl amides are treated with catalyst **1** [33]. One possible explanation for the polymerization of allyl undec-10-enoate (**7**) is that it is achieved *indirectly* via

RCM to give macrocycle **23** followed by an ED-ROMP to give polymer **18**. A CDP of polymer **18** using catalyst **2** and ED-ROMPs involving the metathesis of *substituted* allyl ester moieties in macrocycles **23** and **24** using catalyst **1** or **2** were also successful. As noted above a macrocycle containing an olefinic moiety flanked by two $-\text{CH}_2\text{O}-$ has also been found to undergo ED-ROMP successfully [19].

4. Experimental

Experimental details are as given previously [34]. Catalyst **1** was purchased from Strem Chemicals UK and catalyst **2** from Aldrich Chemicals. Both catalysts were used as received. Reaction solvents were dried and distilled immediately before use. ^{13}C NMR spectra were obtained on a Unity 500 MHz instrument with samples in CDCl_3 . For integrations a “slow pulse” sequence was used (pulse delay 30 s; >200 repetitions)

4.1. Synthesis of allyl esters

Apart from diallyl adipate (**20**), which was a commercial sample, the ester monomers were prepared from the appropriate acid chloride and alcohol in the presence of pyridine using standard procedures [14,35]. All esters had satisfactory FT-IR and ^1H NMR spectra.

4.2. ADMET polymerizations

The following procedure is typical of the ADMET reactions summarized in Table 1.

4.2.1. ADMET polymerization of allyl undecenoate (**7**) (entry 6)

Allyl undecenoate (5.00 g, 22.3 mmol) was placed in a 100 mL round-bottomed flask and the monomer was degassed for 30 min by vigorous stirring under a vacuum (1 mm of Hg). Argon gas was purged into the flask for a further 15 min. Grubbs' catalyst **1** (184 mg, 0.22 mmol, 1 mol%) was then added. A vigorous effervescence occurred as ethene gas was evolved. The mixture was left to stir at 20 °C for 18 h under vacuum. The solid that formed was dissolved in chloroform (10 mL) and the solution evaporated to dryness. Dichloromethane (10 mL), which had been degassed by bubbling argon through it for 1 h, was added plus a fresh portion of catalyst **1** (183 mg) and the solution was stirred at 20 °C for 18 h. During this time most of the dichloromethane evaporated off. The final concentrated solution was then evaporated to dryness and the solution polymerization procedure carried out a second time. The final solution was evaporated to dryness. The solid mass was re-dissolved in a minimum amount of chloroform (25 mL) and precipitated into methanol (500 mL). The sticky precipitate was filtered off and dried in a vacuum oven at 50 °C and 1 mmHg. This gave poly(allyl undecenoate) (**18**) (4.00 g, 91%) as a gray solid. It had $M_n = 14600$, $M_w = 33000$, $M_w/M_n = 2.3$; IR

(CHCl_3) 1638 and 1731 cm^{-1} ; ^1H NMR (CDCl_3) $\delta = 1.20\text{--}1.44$ (m, 10H), 1.56–1.70 (m, 2H), 1.90–2.10 (m, 2H), 2.20–2.40 (m, 2H), 4.48–4.66 (m, 2H) and 5.36–5.90 (m, 2H): there were small peaks at $\delta = 4.7\text{--}5.2$ and 5.6–5.8 due to end-group; ^{13}C NMR $\delta = 25.2, 26.4, 26.5, 27.0, 27.2, 27.4, 27.8, 29.1, 29.4, 29.5, 29.6, 29.9, 32.5, 32.8, 34.0, 34.4, 34.5, 64.0, 65.3, 123.7, 124.1, 128.4, 130.6, 136.7, 173.7, 173.9$.

4.3. Cyclo-depolymerization (CDP) of polymer **18** using Grubbs' catalyst **2**

Polymer **18** (3.84 g, 19.60 mmol) was dissolved in dichloromethane (350 mL), which had been purged with argon for 1 h prior to use. Grubbs' catalyst **2** (166 mg, 1 mol% based on polymer repeat unit) was added and the flask closed. The mixture was stirred gently at 40 °C under a positive pressure of argon for 18 h. The reaction was stopped and the solvent evaporated to give the crude product (3.62 g). The crude mixture was passed through a short alumina column using dichloromethane as solvent. The solvent was evaporated and the residue dried under vacuum at 50 °C and 1 mmHg to give gray waxy mixture of cyclics **23** and **24** (2.69 g, 70%). These had FT-IR (CHCl_3) 1734 cm^{-1} , ^1H NMR (CDCl_3) $\delta = 1.20\text{--}1.44$ (m, 10H), 1.56–1.70 (m, 2H), 1.90–2.10 (m, 2H), 2.20–2.40 (m, 2H), 4.48–4.62 (m, 2H) and 5.30–5.90 (m, 2H): no peaks attributable to end groups were detected; ^{13}C NMR $\delta = 24.8, 24.9, 25.1, 25.3, 25.5, 25.7, 26.1, 26.7, 27.5, 28.4, 28.5, 28.7, 28.8, 28.9, 29.0, 29.1, 29.3, 29.4, 31.6, 32.0, 32.3, 32.8, 34.6, 34.8, 35.3, 63.7, 63.8, 64.8, 65.2, 65.3, 124.3, 124.5, 125.8, 127.9, 130.8, 136.5, 173.6, 173.7$ and 173.8. The MALDI-ToF mass spectrum of the product (dithranol matrix, NaBr) showed mass peaks corresponding from the cyclic dimer [417, dimer + Na, $(M+23)^+$] up to the cyclic pentamer [1002, pentamer + Na, $(M+23)^+$]. The percentage distribution of the cyclics species, by weight, determined by GPC was monomer 41.6%; dimer 20.0%; trimer 11.6%; tetramer 7.4%; pentamer 6.5%; hexamer 5.1%, heptamer 4.6%, higher cyclics 3.2%.

4.4. Entropically driven ring-opening polymerization (ED-ROMP) of the mixture of cyclics **23** and **24**

4.4.1. Using catalyst **1**

The mixture of cyclics obtained in experiment 4.3 (120 mg, 0.61 mmol) and Grubbs' catalyst **1** (25 mg, 0.5 mol%) were dissolved in chloroform to make up a 50% solution in a glass vial. The vial was mounted in an aluminium block and heated in a Buchi oven at 40 °C under argon for 36 h after which time all the solvent had evaporated. The product was analyzed by GPC. It consisted of 95% polymer and 5% oligomers. It was then dissolved in a minimum amount of chloroform and precipitated into methanol. The sample was filtered off then dried overnight in a vacuum oven at 50 °C and 1 mmHg to give a light brown sticky polymer (96 mg, 80%). It had by

GPC M_n 15300 and M_w 32400. The ^1H NMR spectrum was the same as that of poly(allyl undecenoate) (**18**) described in Section 4.2.

4.4.2. Using catalyst **2**

A similar experiment to the above was carried out using the mixture of cyclic oligomers (103 mg; 0.525 mmol) and Grubbs catalyst **2** (2.2 mg, 0.5 mol%) but the reaction was carried out at 40 °C for 12 h. The product (62% yield) after re-precipitation had, by GPC, M_n 12,100, M_w 23450 and it contained < 1% of cyclic oligomers.

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