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Cyclo-depolymerization of olefin-containing polymers to give macrocyclic oligomers by metathesis and the entropically-driven ROMP of the olefin-containing macrocyclic esters

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Abstract

A range of olefin-containing polyesters were prepared by acyclic diene metathesis (ADMET) and were then subjected to cyclo-depolymerization (CDP). CDP involves metathesis of the 1,2-disubstituted olefinic linkages and gives a homologous family of strainless macrocyclic oligomers (MCOs). When Grubbs' "first generation" catalyst was used at 23 °C the CDPs were sluggish and required reaction times of several days, but with the "second generation" Grubbs' catalyst at 40 °C CDPs were complete in only 2–4 h. Macrocyclic olefin-containing lactones were also prepared by ring-closing metathesis. Under appropriate reaction conditions (i.e. neat cyclics or very concentrated solutions of cyclics) the *strainless* macrocycles successfully underwent ring-opening metathesis polymerizations (ROMPs). Unlike most ROMPs reported in the literature, which are usually enthalpically-driven, these ROMPs are entropically-driven (ED-ROMPs). The results obtained clearly demonstrate that 21-, 24-, 27-, 28-, 38-, 45-, 52-, 63-, 64-, 68- and 84-membered macrocycles polymerized successfully. Two of the ED-ROMPs were carried out in films. These ROMPs appeared to proceed in part in the solid phase, i.e. were examples of solid state polymerization.

Keywords: Macrocycles; Ring-closing metathesis; Solid-state polymerization

1. Introduction

Ring:chain equilibria, i.e. the equilibria between macrocyclic oligomers (MCOs) and the corresponding step-growth polymers, see Scheme 1, have been of *theoretical* interest for many years [1–3], but it is only relatively recently that they have begun to find practical applications [4]. The main point of theoretical interest has been the proportions of the members of the homologous families of MCOs present in the cyclic fractions. The most important theory in this context is that of Jacobson and Stockmayer [5]. At its simplest this predicts that if the macrocycles are strainless, the amount of each of the MCOs present decreases progressively as the rings become larger: if the macrocycles are strained they occur in reduced proportions, if at all. In practice, usually >95% by weight of the macrocycles in a family of MCOs consists of rings with from *ca.* 14 to 100 ring atoms, but macrocycles with up to *ca.* 300 ring atoms can often be detected by, for example, mass spectrometry [6]. Thus, essentially all the macrocycles in an equilibrated family of MCOs are strainless.

The equilibrium position of a ring:chain equilibrium is very sensitive to the concentration. At very *high concentrations* it lies heavily in favor of polymer. For example, in a *neat* reaction mixture typically *ca.* 2% of the repeat units are present in the MCOs and *ca.* 98% in polymer. This allows the ring:chain equilibrium to be exploited for a novel type of ring-opening polymerization (ROP). Thus, *if one or more MCO(s) is taken neat and the equilibrium then established, polymer synthesis results*. As most, if not all, the MCOs in the feedstock are strainless the enthalpy change on polymerization is minimal. This type of polymerization is, therefore, mainly entropically-driven [7] and the conversion can be

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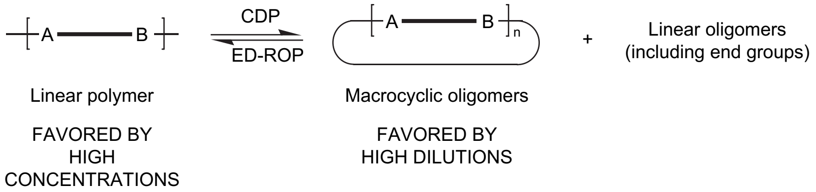


Scheme 1. Ring:chain equilibria. These are concerned with the equilibria between linear polymers and homologous families of the corresponding macrocyclic oligomers.

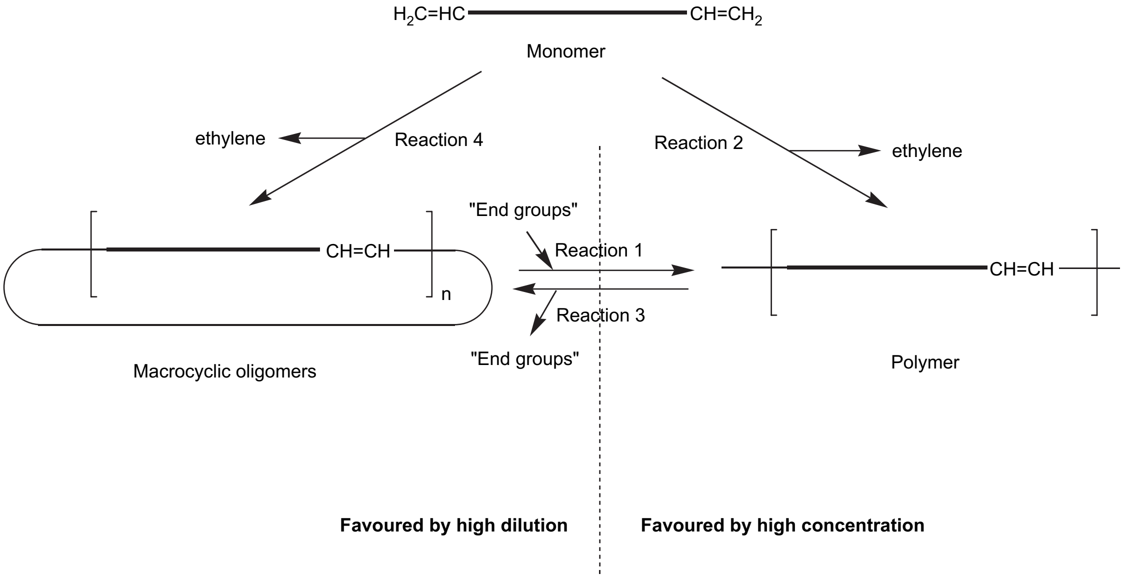
described as an ED-ROP. In the neat mixture of MCOs the macrocycles have relatively little translational entropy and the rings have only limited conformations: conformational flexibility increases greatly upon conversion into polymer. ED-ROPs have several other interesting features [4]. For example, as they just involve a shuffling of the linkages between the repeat units, no volatiles are emitted during the polymerization and little or no heat is evolved. As ED-ROP is an equilibration process the polydispersity index of the product is expected to be 2.0. These features differ from those of most examples of ROP in the literature which generally involve the opening of strained rings, and so are mainly enthalpically-driven [7,8].

In contrast to the above, at *high dilutions* the equilibrium position lies heavily in favor of the MCOs. Often >70%, and sometimes >90%, of the repeat units are present in the MCOs [3,5,9]. This allows ring:chain equilibria to be exploited for polymer degradation. Thus, if a dilute solution of a step-growth polymer, typically *ca.* 2% w/v, is taken and the ring:chain equilibrium established, the polymer degrades to give the MCOs in excellent yield. This process is called cyclo-depolymerization (CDP) or ring-closing depolymerization. It is of interest to note that CDP achieves degradation without the addition of end groups which would then only need to be removed again, often by the use of vigorous reaction conditions [8], in any subsequent condensation polymerization. It is clear that the combination of CDP plus ED-ROP is potentially an attractive means of recycling certain step-growth polymers.

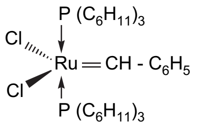
ED-ROPs and CDPs have been studied for many types of polymer, such as polyesters, polyamides, polyurethanes and a wide range of high performance aromatic polymers and the subject has been reviewed several times [4]. However, very few olefin-containing polymers have been studied. One example that has been studied in considerable detail is the polybuta-1,4-diene system [9].

This present paper is concerned with the synthesis of a range of olefin-containing polyesters, the CDP of these polymers to give MCOs with a wide range of ring sizes, and the ED-ROMP (entropically-driven ring-opening metathesis polymerization) of these MCOs. It is also concerned with the synthesis of some olefin-containing macrocyclic lactones by ring-closing metathesis (RCM) [10,11], and the ED-ROMP of these macrocyclic lactones. The relationships between these various reactions are summarized in Scheme 2. The main aim of the present work has been to demonstrate that *large strainless macrocycles* can readily undergo ROMP. A preliminary communication and a brief note on a small part of the subject have been published previously [12,13].

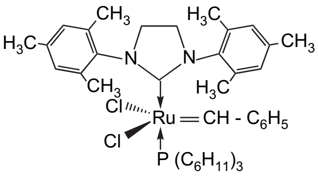
The use of olefin metathesis in polymer chemistry, though long established [14], has greatly increased recently, first with the introduction of Grubbs' "first generation" catalyst **1** [15] and then with the introduction of the "second generation"



Scheme 2. Relationship of various reactions. Reaction 1 is ring-opening metathesis polymerization (ROMP). Reaction 2 is acyclic diene metathesis (ADMET). Reaction 3 is cyclo-depolymerization (CDP). Reaction 4 is ring-closing metathesis (RCM). "End groups" include linear oligomers.



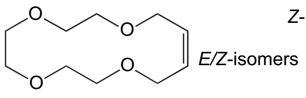
(1)



(2)

Grubbs' catalyst **2** [16]. Both these catalysts are tolerant of many functional groups and they are commercially available. Thus far there has been two major approaches to polymer synthesis using olefin metathesis [14,17]. In one approach [14,18], *strained* cyclic olefins such as norbornene and cyclooctene are subjected to ROMP: see Reaction 1 in Scheme 2. In the other approach [14,19,20], α,ω-divinyl compounds are polymerized by, what is termed, acyclic diene metathesis (ADMET): see Reaction 2 in Scheme 2. The latter are condensation polymerizations where ethylene is the condensate and, because metathesis is reversible, the ethylene must be carefully removed from the reaction system if significant molecular weights are to be obtained. The 1,2-disubstituted in-chain olefinic linkages generated in both these synthetic approaches often undergo, what are termed, secondary metathesis reactions. These olefinic linkages are significantly less reactive than the initial vinyl groups [14], but as the polymerization proceeds they constitute an increasing fraction of the olefinic linkages in the system. Secondary metathesis is important because it can result, for example, in the scrambling of chain lengths. The CDP (see Reaction 3 in Scheme 2) of olefin-containing polymers, discussed below, also involves metathesis of the 1,2-disubstituted olefinic linkages. Literature examples involve the CDP of polybutadiene [9,21]. Other reactions involving these linkages are the depolymerization of polybutadiene [22] and other olefin-containing polymers [23] in the presence of ethylene, and some examples of metathesis degradation in the presence of various functional olefins to give telechelic polymers [24,25].

Examples in which large unstrained MCOs have been subjected to ED-ROMP are rare [9,21,25–30] and there only appears to be two examples where the polymer was formed in high yield and was then isolated and characterized. The first was the ROMP of the 14-membered cyclic ether **3** in the presence of metathesis catalyst **1** [26]. This gave a polymer with M_n 65,900. The second example was the ROMP of ambrettolide (**4**), an unsaturated lactone with 17 ring atoms [27]. A neat sample of this lactone was polymerized using a catalyst prepared from tungsten hexachloride and tetramethyltin to give a polymer in 95% yield with M_n 95,000. Given that Grubbs and coworkers have recently reported a method for the synthesis of very large macrocyclic olefins [31,32] and that olefin-containing polymers are easily hydrogenated in the presence of decomposed metathesis catalysts [33,34], ED-ROMP of large macrocyclic olefins is of more than theoretical interest.



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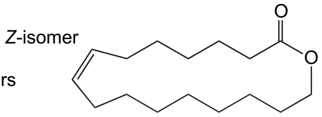


(4)

2. Results and discussion

The main aim of the present work was to obtain further examples of large unstrained macrocyclic olefins undergoing ED-ROMP successfully. A range of such macrocycles were therefore prepared. This required α,ω-bis-olefinic monomers and, in order to have a substantial number of chain atoms (subsequently ring atoms) combined with simple syntheses, α,ω-bis-olefinic esters **5**–**14** were chosen: see Scheme 3. These

$CH_2=CH-(CH_2)_8-CO_2-(CH_2)_9-CH=CH_2$

(5)

$CH_2=CH-(CH_2)_8-CO_2-(CH_2)_m-O_2C-(CH_2)_8-CH=CH_2$

(6): m = 6

(7): m = 16

$CH_2=CH-(CH_2)_8-CO_2-(CH_2)_{10}-O_2C-(CH_2)_8-CH=CH_2$

(8)

$CH_2=CH-(CH_2)_2-O_2C-(CH_2)_2-CO_2-(CH_2)_2-CH=CH_2$

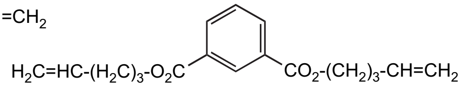
(9)

$CH_2=CH-(CH_2)_9-O_2C-(CH_2)_m-CO_2-(CH_2)_9-CH=CH_2$

(10) : m = 2

(11) : m = 4

(12) : m = 10

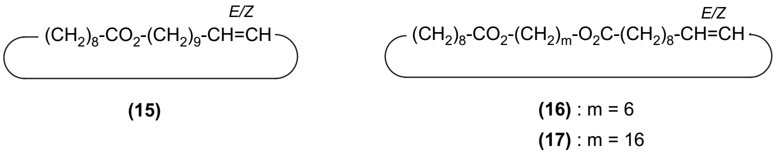


(13)

$CH_2=CH-(CH_2)_2-O-CO-O-(CH_2)_2-CH=CH_2$

(14)

Scheme 3. α,ω-Divinyl monomers used for ADMET polymerization and RCM.



(15)

(16) : m = 6
(17) : m = 16

Scheme 4. Lactones **15−17** prepared by the ring-closing metathesis of compounds **5−7**. Note that compound **16** is the same as **30**: $n = 1$.

esters were prepared from commercial materials by standard methods [35].

Initially a few olefin-containing macrocycles (lactones) were synthesized by ring-closing metathesis (RCM) (see Reaction 4 in Scheme 2) [10,11] and isolated as pure individual compounds. CDP was, however, chosen as the main means to prepare macrocycles because the mixtures of MCOs obtained from CDP are expected to contain a significant fraction of rings with up to 100 ring atoms. Also, the use of CDP means the MCOs can be prepared in good yields with little or no contamination by linear oligomers. The latter is the case because, apart from groups introduced as part of the catalyst, the product cannot contain more end groups than the original starting material. If, for example, a linear polymer chain with a degree of polymerization of 100 is converted into oligomers with an average degree of polymerization (DP) of 4, then 25 oligomer molecules are formed from the chain. However, only one pair of end groups was present on the original chain so there are only sufficient end groups for one of the oligomer molecules to be linear, i.e. in this example, one in 25 molecules is linear. Accordingly, a series of olefin-containing polymers were prepared and subjected to CDP.

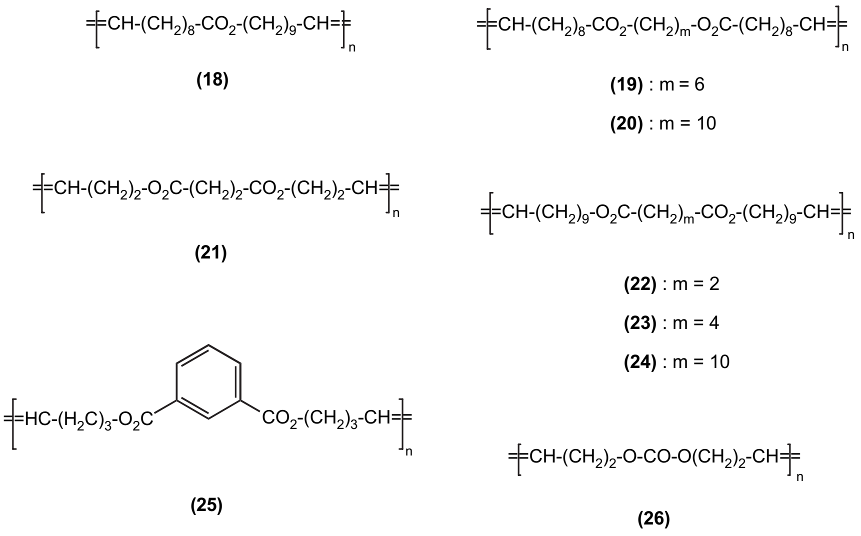
The ED-ROMP of the macrocyclic olefin-containing lactones and the various MCOs was then studied.

2.1. Synthesis of macrocyclic lactones by ring-closing metathesis

Three pure macrocyclic monomers, namely compounds **15−17**, were prepared, from the α,ω-divinyl compounds **5−7**, respectively, by RCM [10,11]: see Scheme 4. Dilute solutions of the α,ω-divinyl compounds in dichloromethane at 25 °C were treated with 3 mol% of Grubbs' catalyst **1**. After careful chromatography the required compounds **15−17** were isolated, albeit in modest overall yields (19−56%). These contained 21, 28 and 38 ring atoms, respectively. It is interesting to note that whilst for the larger rings the percentage of the *E*-isomer was *ca.* 80%, for compounds **15** the percentage of the *E*-isomer was only 45%. Comparable figures have been obtained by other workers [36].

2.2. Synthesis of olefin-containing polyesters

The majority of the olefin-containing polymers used in the present study were prepared by ADMET [20] from esters **5**, **6** and **8−13** and carbonate **14**. Each ADMET was carried out in two stages. First the neat monomer was treated for 24 h with 1 mol% of Grubbs' catalyst **1** at 25 °C under a vacuum. Then the viscous product so obtained was dissolved in a small amount of dichloromethane at 25 °C and treated with a fresh portion of catalyst **1** for a further 24 h. The product was isolated by precipitation into methanol and was characterized by FTIR spectroscopy, ^{1}H NMR spectroscopy and gel permeation chromatography (GPC). The results for polymers **18−26**, see Scheme 5, are summarized in Table 1. It is evident that most polymers had M_n values of 5000−20,000. These values are sufficiently large to make CDP straightforward (see above regarding the potential presence of linear oligomers). The proportions of the *E*- and *Z*-isomers were determined by ^{13}C NMR



(18)

(19) : m = 6
(20) : m = 10

(21)

(22) : m = 2
(23) : m = 4
(24) : m = 10

(25)

(26)

Scheme 5. Polymers **18−26** prepared by ADMET polymerization. The proportions of *E*- and *Z*-linkages are as given in Table 1. Polymer **18** can have head-to-head, tail-to-tail and head-to-tail linkages.

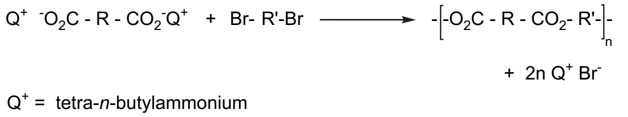
Table 1
Synthesis of polymers **18–26** by ADMET of α,ω-dienes **5**, **6**, and **8–14** using Grubbs' catalyst **1**[a]

Entry	Monomer	Polymer	Yield[b] (%)	Molecular weights × 10^{-3}[c]		PDi	T_g/T_m (°C)	% *E*-isomer[d]
				M_n	M_w			
1	**5**	**18**	86	5.40	9.20	1.7	–/57	82
2	**6**	**19**	90	19.90	38.00	1.9	−36/59	82
3	**8**	**20**	78	19.20	40.40	2.1	–	82
4	**9**	**21**	57	5.30	9.50	1.8	−36/52	70
5	**10**	**22**	70	4.55	8.55	1.9	–	–
6	**11**	**23**	91	10.30	22.40	2.2	–/58	82
7	**12**	**24**	88	17.50	43.10	2.5	–	81
8	**13**	**25**	92	15.70	31.60	2.0	−16/85	85
9	**14**	**26**	48	6.70	11.60	1.7	−40/59	72

[a] See Section 4 for full details of the reaction procedure.
[b] After reprecipitation.
[c] By GPC versus polystyrene standards.
[d] Percentage of *E*-isomer; remainder is *Z*-isomer. Determined by ^{13}C NMR spectroscopy.

spectroscopy and found to be 70–82% of the *E*-isomer and 30–18% of the *Z*-isomer. These values are essentially those expected for a thermodynamically equilibrated mixture of geometrical isomers. In several cases T_gs and T_ms were determined by differential scanning calorimetry. All the T_gs determined were less than 0 °C and the highest T_m was only 85 °C.

An alternative synthetic route was investigated briefly for three polymers. Thus, polymers **18**, **19** and **24** were each synthesized by phase transfer catalysed reactions between a dibromide and a diacid in the presence of tetra-*n*-butylammonium hydroxide [37]: see Reaction 5. The required diacid **27** was prepared *via* the self-metathesis of methyl undec-10-enoate and the dibromide **28** was prepared similarly from undec-10-enyl bromide. The results obtained are summarized in Table 2. Although the molecular weights obtained are only modest, they were nevertheless sufficient for CDP (see above). This demonstrates that the required olefin-containing polymers do not always have to be prepared by ADMET polymerization.



Reaction 5.

$$HO_2C\text{-}(CH_2)_8\text{-}CH\overset{E/Z}{=}CH\text{-}(CH_2)_8\text{-}CO_2H$$

(27)

$$Br\text{-}(CH_2)_9\text{-}CH\overset{E/Z}{=}CH\text{-}(CH_2)_9\text{-}Br$$

(28)

2.3. *Cyclo-depolymerization of the olefin-containing polyesters **18–25** and polycarbonate **26***

CDPs were carried out using the olefin-containing polymers **18–26** described above. The results are summarized in Table 3. Initially the CDP of polymer **19** was carried out by treating a 1% w/v solution of the polymer in dichloromethane at 23 °C with 1 mol% of Grubbs' catalyst **1**; see Table 4. It was fully expected that the reaction would be sluggish because it involved the 1,2-disubstituted in-chain olefinic linkages. The reaction was monitored by GPC and it was found that to obtain a good yield of MCOs the CDP needed to be carried out for several days. During this period fresh catalyst was added if the GPC analyses suggested the reaction had slowed significantly. Following this experiment several other polymers were subjected to CDP under similar reaction conditions. In each case at the end of the reaction period the reaction mixture was analyzed by GPC. The results of these analyses are given in Table 3, entries 2, 4, 8, 9 and 11. The MCOs **29–37**, see Scheme 6, were then isolated by passing the reaction products

Table 2
Synthesis of olefin-containing polyesters **18**, **19** and **24** by phase transfer catalysed Reactions 3[a]

Entry	Polymer synthesized	Diacid	Dihalide	Yield (%)	Molecular weights × 10^{-3}[b]		PDi	DP[c]
					M_n	M_w		
1	**18**	**27**	**28**	80	8.20	14.70	1.8	14
2	**19**	**27**	1,6-Dibromohexane	51	4.10	6.30	1.5	10
3	**24**	1,10-Decanedicarboxylic acid	**28**	74	6.90	13.10	1.9	15

[a] See Section 4 and Ref. [37] for full experimental details.
[b] By GPC in comparison with polystyrene standards.
[c] Calculated from the value for M_n. A repeat unit is considered to be the moiety derived from one of each type of monomer unit.

Table 3
Cyclo-depolymerization of olefin-containing polyesters **18–26** using various catalysts[a]

Entry	Polymer	Catalyst[b]	Ring atoms per repeat unit	MCOs	Yield[c] (%)	Composition of the product[d]						MALDI[e]
						$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n > 5$	Polymer	
1	**18**[f]	G2	21	**29**	51	52	30	7	4	5	2	2 and 3
2	**19**[g]	G1	28	**30**	73	41	19	10	7	13	10	1–5
3	**19**	G2	28	**30**	84	43	21	11	8	10	7	1–6
4	**20**	G1	32	**31**	59	26	13	9	7	19	26	1–6
5	**20**	G2	32	**31**	52	48	16	8	6	10	12	1–8
6	**21**	G2	12	**32**	92	0	88	9	2	1	–	2–4
7	**22**	G2	26	**33**	80	72	18	6	1	–	4	1–4
8	**23**	G1	28	**34**	88	40	17	9	7	15	12	1–6
9	**24**[h]	G1	34	**35**	74	20	10	8	6	5	51	1–5
10	**24**	G2	34	**35**	95	45	15	8	6	12	14	1–5
11	**25**	G1	15	**36**	57	32	16	8	5	7	16	2–6
12	**26**	G2	9	**37**	97	0	70	12	6	8	4	2–6
13	**18**	BTO	21	**29**	70	40	16	7	3	4	30	–
14	**18**	DBDBT	21	**29**	93	50	23	10	5	3	9	–

[a] See Section 4 for full experimental details.

[b] G1 = experiment used catalyst **1** in dichloromethane at 23 °C for 9 days; G2 = experiment used catalyst **2** in chloroform at 40 °C for 4 h; BTO = experiment used di-*n*-butyltin oxide in chlorobenzene at 133 °C for 9 days; DBDBT = experiment used dibutoxydibutyltin in chlorobenzene at 133 °C for 10 h.

[c] Yield of MCOs after passing product through a short column of alumina.

[d] By GPC using a column designed to separate oligomers. Analyses refer to the composition of the crude reaction product. After passage through the alumina column the proportions of the MCOs were unchanged.

[e] MALDI-ToF mass spectra showed clear peaks due to a homologous family of MCOs for the range shown.

[f] The corresponding polymer **18** prepared using phase transfer catalysis gave with catalyst **1** the MCOs in 72% yield and the composition of the product was $n = 1$, 34%; $n = 2$, 18%; $n = 3$, 9%; $n = 4$, 17%; $n = 5$, 7% with 22% polymer.

[g] The corresponding polymer **19** prepared using phase transfer catalysis gave with catalyst **1** the MCOs in 75% yield and the composition of the product was $n = 1$, 43%; $n = 2$, 11%; $n = 3$, 13%; $n = 4$, 11%; $n = 5$, 6% with 16% polymer.

[h] The corresponding polymer **24** prepared using phase transfer catalysis gave with catalyst **1** the MCOs in 78% yield and the proportions of the product was $n = 1$, 27%; $n = 2$, 15%; $n = 3$, 11%; $n = 4$, 9%; $n = 5$, 12% with 26% polymer.

down a short column of active alumina to remove the catalyst residues and any high molecular weight polymer. The MCOs were characterized by FTIR spectroscopy (lack of vinyl groups), ^{1}H NMR spectroscopy (lack of vinyl end groups), GPC and MALDI-ToF mass spectrometry. A typical GPC trace and MALDI-ToF MS are shown in Figs. 1 and 2a, respectively. After the MCOs were isolated the proportions of the various homologs were the same as in the crude reaction products.

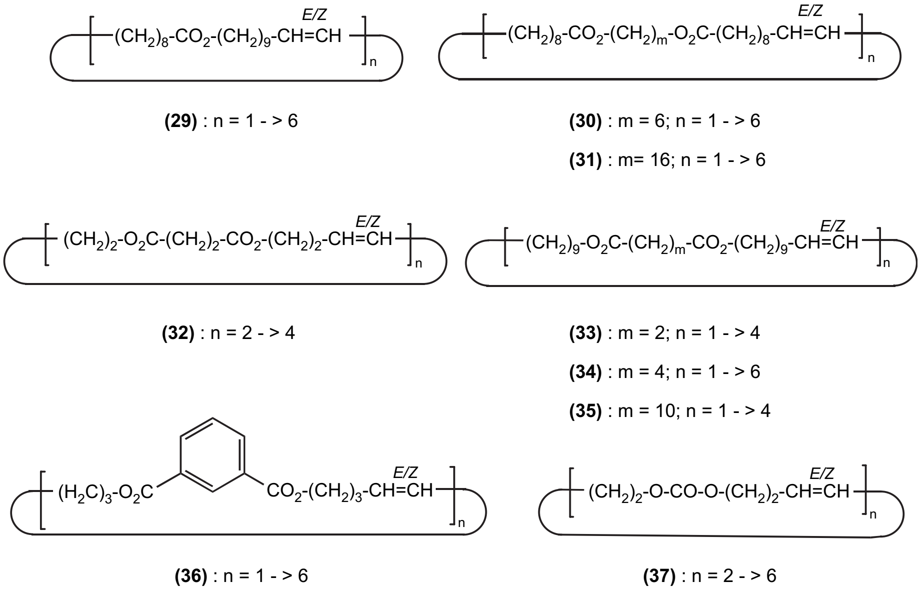
Subsequently CDPs were also carried out using the "second generation" Grubbs' catalyst **2**. This catalyst has been reported to be more active than catalyst **1** in various reactions [16,38–42]. Initially trial experiments were carried out with polymer **19** using catalyst **2** at 23 °C and at 40 °C. The results are summarized in Table 4. It is evident that catalyst **2** is more effective than catalyst **1** for CDP, especially when used at 40 °C. Thus, whereas with catalyst **1** a reaction time of several days at 23 °C was required to obtain a satisfactory yield of MCOs, with catalyst **2** a high yield could be obtained in only 2 h at 40 °C. Accordingly further CDPs were carried out using catalyst **2** at 40 °C, but with a reaction time of 4 h to ensure the reaction reached equilibrium: see Table 3 entries 1, 3, 5–7, 10 and 12. The MCOs **30–33**, **35** and **37** were isolated and characterized as before.

Table 4
CDP of polymer **19** using catalysts **1** and **2** under various conditions[a]

Entry	Time (h)	Catalyst **1** at 23 °C		Catalyst **2** at 23 °C		Catalyst **2** at 40 °C	
		% MCOs	% Polymer	% MCOs	% Polymer	% MCOs	% Polymer
1	1	45	55	80	20	91	9
2	2	63	37	93	7	93	7
3	4	69	31	–	–	–	–
4	8	73	27	–	–	–	–
5	24	74	26	93	7	93	7
6	216	90	10	–	–	–	–

[a] All the percentage compositions were determined by GPC using the column specially prepared to resolve oligomers. All the reactions were carried out using a 1% solution of the polymer in dichloromethane under an argon atmosphere and using 1 mol% of catalyst.

It is of interest to compare the MALDI-ToF MS of the MCOs obtained using catalysts **1** and **2**, because it has been reported recently that treatment of olefins with catalyst **2** can cause the olefinic bond to migrate [43–45]. The MS obtained for the MCOs **30** obtained using catalyst **1**, shown in Fig. 2a, has clean signals attributable to the cyclic monomer up to the cyclic tetramer. This indicates that both the ADMET synthesis of polymer **19** and the subsequent CDP using catalyst **1** take place without C=C migration. The MS obtained for the MCOs **30** obtained using catalyst **2** is shown in Fig. 2b. In contrast to that shown in Fig. 2a all the mass peaks have satellites at 14 amu intervals indicating C=C migration occurred during the CDP. For example, near the major peak for [cyclic dimer plus Na^{+}] at 868 amu there are smaller peaks indicating CH_2 loss at 854 and 840 amu, and peaks indicating CH_2 gains at 882 and 896 amu. The intensities of these peaks suggest that *ca.* 35% of the cyclic dimer is a product of C=C migration. With the GPC equipment available to us, the GPC trace of the product obtained using catalyst **2** is indistinguishable



Scheme 6. Macrocyclic oligomers prepared by cyclo-depolymerization.

from that obtained using catalyst **1**. Although the former catalyst gave a more complex product, to simplify the ensuing discussion such MCOs will be referred to as simple oligomer products. It should be noted, however, that when catalyst **1** is used, although the reactions are slower, the products do not have these structural variations.

The compositions of the MCO fractions are of interest and two points are to be noted. First, the compositions of the MCOs obtained using catalyst **2** follow the expected pattern [5], i.e. very little, if any, of the smaller rings are present if they are strained, see entries 6 and 12, then, once the rings are strainless, they progressively decrease in amount as they increase in size. Numerically the percentage compositions are very similar to those obtained from the CDPs of simple aliphatic polyesters [46,47]. Second, the compositions of the MCOs obtained using Grubbs' catalyst **1** are sometimes significantly different to those obtained using Grubbs' catalyst **2**: compare, for example, Table 3 entries 4 and 5. This is almost certainly because the CDPs using catalyst **1**, whilst they had reached the point of producing a high yield of MCOs, still had not reached full equilibrium.

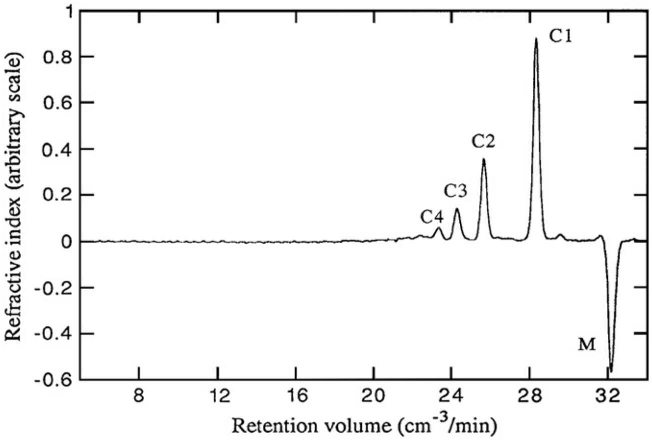


Fig. 1. GPC of the MCOs **30** obtained by the CDP of polymer **19** using catalyst **1** (experiment summarized in Table 3, entry 2). The "oligomer" GPC column was used. "M" is a *n*-dodecane marker.

Attempts were also made to carry out CDP *via* transesterification rather than *via* olefin metathesis [4]. Di-*n*-butyltin oxide (2 mol%) in chlorobenzene at 133 °C for 8 h [46] and in 1,2-dichlorobenzene at 183 °C for 72 h [48] have proved to be effective systems for such CDPs in earlier studies and in the present study similar conditions were used to carry out the CDP of polymer **18** prepared by ADMET. The CDP, however, proved to be extremely sluggish requiring a reaction time of 9 days at 183 °C to obtain a satisfactory yield, see Table 3 entry 13. In contrast, the CDP of polyundecanoate (prepared from 11-bromoundecanoic acid and tetra-*n*-butylammonium hydroxide by a phase transfer catalysed reaction) required only 8 h at 133 °C [46]. Since polyesters prepared using tetra-*n*-butylammonium hydroxide generally have hydroxyl end groups on many of the chains, this result is consistent with the view that to be effective the di-*n*-butyltin oxide needs to first react with hydroxyl end groups [49]: backbiting then ensues. The present polymer **18**, however, by virtue of its method of synthesis has only vinyl end groups. In contrast, when di-*n*-butoxydi-*n*-butyltin (**38**) (2 mol%) was used as the transesterification catalyst at 133 °C [46], the CDP of polymer **18** proceeded in high yield in just 10 h. The composition of the MCO fraction was similar to that obtained by the CDP by metathesis: see Table 3 entries 1 and 14. Thus the CDP of polymer **18** can be achieved using either olefin metathesis or transesterification.

$(n\text{-}C_4H_9O)_2\ (n\text{-}C_4H_9)_2Sn$

(38)

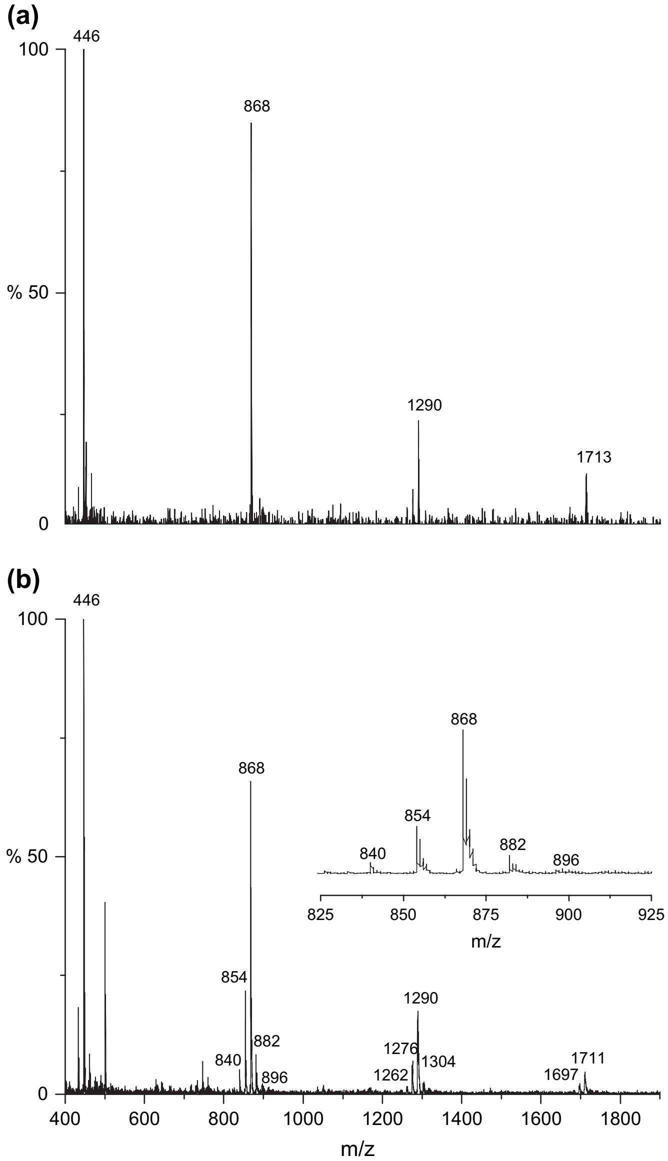


Fig. 2. (a) MALDI-ToF mass spectrum of the MCOs **30** obtained by the CDP of polymer **19** using catalyst **1** (experiment summarized in Table 3, entry 2). (b) MALDI-ToF mass spectrum of the MCOs **30** obtained by the CDP of polymer **19** using catalyst **2** (experiment summarized in Table 3, entry 3). In both cases the matrix was dithranol doped with sodium bromide. In both cases the major mass peaks are due to [nM + Na$^+$] where n = 1–4.

2.4. *Entropically-driven ring-opening metathesis polymerization of olefin-containing macrocyclic esters*

The main aim of the work described in this paper was to demonstrate that ROMP of macrocyclic *strainless* olefins can be carried out successfully using appropriate reaction conditions. The results of the various polymerizations are summarized in Table 5.

Initially ED-ROMPs of MCOs **30** were investigated using Grubbs' catalyst **1**. First a 40% w/v solution in dichloromethane containing 1 mol% of catalyst **1** was stirred at 25 °C under an argon atmosphere. The solvent was allowed to evaporate over 3 h. Thus, the reaction mixture began as a highly concentrated solution but became neat with the loss of the solvent. The progress of the polymerization was monitored by GPC. As expected the ring:chain equilibrium shifted gradually to favor polymer **19**. After 2 h the ratio of MCOs to polymer was 19:81, and after 4 h it was 11:89. After 12 h it was 5:95 and it subsequently did not change further. Thus equilibration had been achieved. The molecular weight data obtained at this stage are given in Table 5 entry 6. In the light of these results, three other MCOs in dichloromethane were treated with 1 mol% of catalyst **1** at 25 °C for 12 h following the same general procedure: see Table 5 entries 5, 11 and 13. ED-ROMPs occurred satisfactorily with MCOs **29** and **34**, see entries 5 and 11, but metathesis was sluggish with MCOs **36**, see entry 13. The reason for the latter is not clear but they are the only MCOs with aromatic residues.

In view of the effectiveness of catalyst **2** at achieving CDP, ED-ROMPs of MCOs were also studied using this catalyst. A similar procedure to that described above was used except the starting solution was 50% w/v in chloroform, 1 mol% of catalyst **2** was used and the reaction temperature was 40 °C. The results, summarized in Table 5 entries 8–10, 12 and 14, again indicate that ED-ROMPs occurred satisfactorily. It must be borne in mind, however, both here and elsewhere, that when catalyst **2** is used to catalyse ROMP the products are likely to have a series of closely related repeat units.

The pure lactones **15–17** were also polymerized using 1 mol% of catalyst **2** at 40 °C to give products **18**, **19** and **39**: see Table 5, entries 1–3. In two cases the polymerizations were complete in only 10 min. These results clearly demonstrate that ED-ROMP can be carried out successfully with 21-, 28- and 38-ring lactones.

$$=\!\left[\mathrm{CH{-}(CH_2)_8{-}CO_2{-}(CH_2)_{16}{-}O_2C{-}(CH_2)_8{-}CH{=}}\right]_n\!=$$

(39)

Finally solvent cast films of lactone **17** containing 1 mol% of catalyst **2** and MCOs **30** containing 1 mol% of catalyst **1** were prepared on microscope slides. In each case, after 10 min at 40 °C the solvent had evaporated off and a polymeric film had formed that could be peeled off to give a self-standing film. The films were analyzed by GPC: see Table 5 entries 4 and 7, respectively. This demonstrates the potential of ED-ROMP to be used to form coatings without the evolution of volatiles. It seems very likely that these ROMPs in films are, towards the ends of the reactions, examples of solid state polymerizations. It will be noted that the polymerization temperatures are above the T_gs but below the T_ms of the polymers (see Table 1, entry 2 and Table 5, footnote h). Recently Wagener et al. have reported that ADMET polymerizations can take place in the solid phase [49].

In all the cases of ED-ROMP discussed above except one (entry 13) the ring:chain equilibrium shifted to heavily favor the polymer (usually > 96%) but, as expected, when equilibrium had been established small amounts of MCOs still remained. It should be remembered that the products of most

Table 5
Synthesis of polymers **18**–**26** by ED-ROMP of cyclics **5**–**7** and **29**–**37** and using Grubbs' catalysts **1** or **2**[a]

Entry maximum	Macrocyclic oligomer or MCOs[b]	Ring atoms per repeat unit	Reaction conditions[a]	Polymeric product	Composition of product[c]		Molecular weights[d] × 10^{-3}		PDi	Ring size polymerized[e]
					% Cyclics	% Polymer	M_n	M_w		
1	**15**	21	G2, 12 h, 40 °C	**18**[f]	4	96	37.0	67.5	1.8	21
2	**16**	28	G2, 10 min, 40 °C	**19**[f]	6	94	55.0	105.0	1.9	28
3	**17**	38	G2, 10 min; 40 °C	**39**[f]	4	96	80.4	159.0	2.0	38
4	**17**	38	G2, 15 min, 40 °C[g,h]	**39**[f]	10	90	103.0	207.0	2.0	38
5	**29**	21	G1, 12 h, 25 °C	**18**	3	97	20.1	42.1	2.1	63
6	**30**	28	G1, 12 h, 25 °C	**19**	4	96	20.9	43.4	2.0	84
7	**30**	28	G1, 15 min, 40 °C[g]	**19**	4	96	38.9	74.1	1.9	84
8	**31**	32	G2, 12 h, 40 °C	**20**[f]	4	96	33.7	64.3	1.9	64
9	**32**	12	G2, 12 h, 40 °C	**21**[f]	8	92	15.0	28.8	1.9	24
10	**33**	26	G2, 12 h, 40 °C	**22**[f]	1	99	10.6	23.2	2.2	52
11	**34**	28	G1, 12 h, 25 °C	**23**	3	97	12.0	30.3	2.5	84
12	**35**	34	G2, 12 h, 40 °C	**24**[f]	4	96	19.1	41.8	2.2	68
13	**36**	15	G1, 12 h, 25 °C	**25**	25	75	12.2	22.5	1.8	15
14	**36**	15	G2, 12 h, 40 °C	**25**[f]	3	97	13.1	29.5	2.3	45
15	**37**	9	G2, 12 h, 40 °C	**26**[f]	2	98	21.2	42.4	2.0	27

[a] See Section 4 for full details of the reaction procedures.
[b] Entries 1–4 are experiments used pure macrocyclic monomers; entries 5–15 used mixtures of MCOs.
[c] By GPC analysis. The reaction products were recovered quantitatively.
[d] By GPC versus polystyrene standards.
[e] See text for method of calculation.
[f] Products may have various closely related repeat units due to C=C migration: see text.
[g] Reaction carried out as a film on a microscope slide.
[h] By DSC polymer **39** had T_g −32 °C and T_m 65 °C.

conventional step-growth polymerizations contain *ca.* 2% by weight of a mixture of MCOs [50]. It is not clear why the polymerization of MCOs **36** summarized in entry 13 was less successful. The number average molecular weights (M_n) obtained using the MCOs as starting materials were generally in the range 10,000–34,000 whilst those obtained using the pure lactones were in the range 37,000–103,000. It is interesting to note that in most cases these values are significantly higher than those obtained for the syntheses of the same polymers using ADMET: see Table 1. This is probably because in ADMETs removing the ethylene *completely* is not always easy: in contrast the ED-ROMP systems contain relatively few potential end groups. The higher M_ns obtained using the pure lactones is probably due to them being more pure than the MCOs prepared by CDP, i.e. the latter may contain traces of linear oligomers. The polydispersities were expected to be 2.0. In practice they were usually in the range 1.8–2.5.

At this stage none of the above polymers had been reprecipitated. Firstly, this was because we wished to demonstrate that though the polymerizations had proceeded in high yield small amounts of MCOs remained. Secondly, in the case of the polymerizations starting from homologous families of MCOs, it made it possible to determine which of the macrocycles had actually undergone ED-ROMP. We believe that the combined experimental and analytical errors in determining the compositions of the initial feedstock and of the final product amount to less than 5%. Thus, any MCO present in the feedstock more than 5% in excess of the amount of MCOs recovered must have polymerized. The results of these calculations are shown in the final column of Table 5, entries 5–12, 14 and 15. The results demonstrate that in the various polymerizations up to 24-, 27-, 45-, 52-, 63-, 64-, 68- and 84-membered macrocycles successfully underwent ED-ROMP.

Reprecipitation of the polymers was not trivial because most of the polymers had low T_ms, see Table 1, and so were not easily obtained as solids. Polymers **20**, **21** and **24** were, however, reprecipitated successfully from chloroform solutions into methanol at 0 °C. The products were then analyzed by GPC. The results are summarized in Table 6. As expected the molecular weights increased and the percentages of the

Table 6
Comparison of selected polymers prepared by ED-ROMP before and after reprecipitation[a]

Entry	Polymer	Analysis before precipitation				Analysis after precipitation			
		Polymer present[b] (%)	Molecular weights[b]		PDi	Polymer present[b] (%)	Molecular weights[b]		PDi
			M_n	M_w			M_n	M_w	
1	**20**	96	33.7	64.3	1.9	98	35.8	67.2	1.9
2	**21**	92	15.0	28.8	2.0	99	18.3	33.3	1.8
3	**24**	96	19.1	41.8	2.3	98	20.7	47.8	2.3

[a] See Section 4 for full details of the reaction procedures.
[b] By GPC versus polystyrene standards.

MCOs in the products decreased to <2% by weight. Reprecipitation also resulted in lighter colored products [51]. The products were characterized by FTIR spectroscopy, ^{1}H NMR spectroscopy, and ^{13}C NMR spectroscopy. Finally, it was demonstrated that heating *dilute* solutions of the reprecipitated products in dichloromethane did not convert any of the polymer back in to MCOs, i.e. after reprecipitation the catalyst had been totally removed and/or any traces of catalyst that remained had lost activity.

Finally, a useful practical feature of ED-ROPs is that because the rings are large they can include substantial structural features. Very recently, since the work described in this paper was completed, a group in Montreal has provided an example. They used ED-ROMP to prepare polymers containing lithocholic acid moieties in the rings [52].

3. Conclusions

The main aim of the present project was to demonstrate that under appropriate reaction conditions (neat or very concentrated solutions of cyclics) ED-ROMP can be carried out successfully with *strainless* macrocycles. This paper reports examples of 15 successful ED-ROMPs. The results obtained with lactones **15–17** clearly demonstrate that 21-, 28- and 38-membered macrocycles polymerize well. Similarly the results with the various mixtures of MCOs demonstrate that up to 84-membered macrocycles can be polymerized. It is also clear ED-ROMP can be carried out successfully in films, possibly in part by solid state polymerizations.

CDP of the olefin-containing polyesters is sluggish and when Grubbs' "first generation" catalyst **1** is used at 23 °C and it requires a reaction time of several days. With the "second generation" Grubbs' catalyst **2** at 40 °C CDP was complete in only 2–4 h. This paper reports examples of 12 successful CDPs that proceed *via* olefin metathesis. With catalyst **1** no migration of the olefinic groups took place but there is MS evidence it did when catalyst **2** was used.

CDP plus ED-ROP has the potential to be an attractive method for recycling certain polymers. Unlike some other forms of depolymerization, CDP achieves depolymerization without introducing many end groups, groups that would only have to be removed again, often with considerable difficulty, if the polymer were to be resynthesized.

4. Experimental

4.1. General considerations

Unless otherwise stated, starting materials were purchased from the Aldrich Chemical Company or Lancaster Synthesis Ltd and were used without further purification. All reactions requiring an inert atmosphere were carried out under dry argon. Organic solutions were dried using magnesium sulfate. Infrared spectra were measured using an ATI Mattson Genesis series FTIR spectrometer either as KBr discs or as films cast from chloroform solutions on to NaCl plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA 300 MHz 'Athos' instrument for solutions in $CDCl_3$. Chemical shifts are quoted in parts per million (ppm) downfield from tetramethylsilane (TMS). Matrix assisted laser desorption ionization time of flight mass spectra (MALDI-ToF MS) were obtained using a Micromass ToF Spec 2E spectrometer equipped with a nitrogen laser operating at 337 nm with a 4 ns pulse width. The matrix employed was dithranol doped with sodium bromide. GPC analyses of *polymers* were carried out using an in-house-assembled instrument equipped with a Knauer 64 pump operating at a flow rate of 1 cm^{3} of tetrahydrofuran per minute through a PL Gel 30 cm 10μ Mixed-B (×2) and 500A (×1) three-column set followed by a Gilson 132 differential refractometer for detection. The system was calibrated using a series of polystyrene standards, each with a narrow polydispersity. GPC analyses of *oligomers* were carried out using an in-house-assembled instrument equipped with a Waters M45 pump operating at a flow rate of 1 cm^{3} of tetrahydrofuran per minute through a Waters Styragel HR1, 2 and 3 three-column set followed by a Gilson 132 differential refractometer for detection. DSC measurements were carried out on a Seiko SSC/5200 machine operating at a heating rate of 10 °C/min in a nitrogen atmosphere. T_g and T_m values were taken on second heating scans, and were taken as the midpoints of the transitions.

4.2. Synthesis of bis(but-3-enyl) carbonate (*14*)

But-3-en-1-ol (15.00 g, 208.0 mmol), dimethyl carbonate (8.43 g, 93.5 mmol) and LiH (30.0 mg, 2.5 mmol, 0.2 wt%) were mixed together in a round-bottomed flask that had been purged with argon. The mixture was stirred and heated at 90 °C and methanol was distilled off until no more was recovered. The reaction was then connected to a vacuum and the distillation continued for another 2 h. The residue was dissolved in hexane (200 mL) and flashed through a short column of alumina. Evaporation of the solvent gave monomer **14** as a viscous colourless oil (11.03 g, 70%). It had IR (cast film) 1746 and 1642 cm^{-1}; ^{1}H NMR δ 2.40–2.50 (m, 4H), 4.18–4.24 (t, $J = 6.74$ Hz, 4H), 5.08–5.24 (m, 4H) and 5.76–5.90 ppm (m, 2H). Anal. Calcd for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 61.8; H, 8.60%.

4.3. Synthesis of lactones *15–17* by ring-closing metathesis

The following procedure is typical.

4.3.1. Synthesis of lactone *15*

Solutions of ester **5** (1.35 g, 4.00 mmol) and of Grubbs' catalyst **1** (99 mg, 0.12 mmol), each in dichloromethane (100 mL), were simultaneously added to vigorously stirred dichloromethane (200 mL) over a period of 8 h at 20 °C. After stirring for 24 h a small sample was analyzed by GPC (oligomer column). Fresh catalyst (3 mol%) was added and the mixture stirred for a further 24 h. The solvent was then evaporated off in vacuo and the residue chromatographed over a silica column using petroleum ether/dichloromethane mixture (equal volumes) as eluant. This afforded lactone **15** (230 mg, 19%) as a clear colourless oil. Analysis by GPC (oligomer column) showed only one peak. The oil had IR (cast film) 1736 cm^{-1}; ^1H NMR δ 1.20–1.44 (bs, 22H), 1.60–1.70 (m, 4H), 2.00–2.10 (m, 4H), 2.36 (t, $J = 6.32$ Hz, 2H), 4.10–4.20 (m, 2H) and 5.35–5.45 ppm (m, 2H), there were no signals attributable to vinyl groups; ^{13}C NMR δ 25.1, 25.8, 26.1, 26.5, 26.6, 27.7, 27.9, 28.2, 28.4, 28.5, 28.7, 28.8, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 31.7, 31.9, 34.4, 34.7, 63.9, 64.1, 129.9 and 130.0 (*cis*, 55%) and 130.8 (*trans*, 45%), 173.8 and 173.9 ppm. Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.92; H, 11.69. Found: C, 77.61; H, 11.45%.

4.3.2. Lactone **16**

Lactone **16** was prepared using the same procedure as that described above for lactone **15** but using 1,6-hexanyl bis(undec-10-enoate) (**6**) (1.08 g, 2.40 mmol), Grubbs' catalyst **1** (59 mg, 0.072 mmol) and dichloromethane (400 mL). The product was passed through a silica column using a dichloromethane/petroleum ether mixture (9 vol:1 vol) as eluant. This afforded lactone **6** (330 mg, 33%) as a clear colourless oil. Analysis by GPC (oligomer column) showed only one peak. The oil had IR (cast film) 1736 cm^{-1}; ^1H NMR δ 1.20–1.46 (m, 24H), 1.54–1.70 (m, 8H), 1.93–2.05 (m, 4H), 2.25–2.33 (t, $J = 7.42$ Hz, 4H), 4.05–4.10 (t, $J = 6.32$ Hz, 4H), 5.32–5.38 ppm (m, 2H), there were no peaks attributable to vinyl end groups; ^{13}C NMR δ 25.0, 25.7, 26.9, 28.4, 28.6, 28.9, 29.0, 29.1, 29.5, 32.2, 34.5, 64.1, 129.9 (*cis*, 20%), 130.5 (*trans*, 80%) and 173.9 ppm. Anal. Calcd for $C_{26}H_{46}O_4$: C, 73.93, H, 10.90. Found: C, 74.35; H, 10.96%.

4.3.3. Lactone **17**

Lactone **17** was prepared using the same procedure as that described above for compound **15** but using 1,16-hexadecanyl bis(undec-10-enoate) (**7**) (0.885 g, 1.50 mmol), catalyst **1** (37 mg, 0.045 mmol) and dichloromethane (250 mL). The product was passed through a silica column using dichloromethane/petroleum ether mixture (65:35) as eluant. This afforded lactone **17** (0.47 g, 56%) as a white solid, mp = 68–69 °C. Analysis by GPC (oligomer column) showed only one peak. It had IR (cast film) 1734 cm^{-1}; ^1H NMR δ 1.20–1.44 (m, 48H), 1.58–1.70 (m, 8H), 1.94–2.04 (m, 4H), 2.30–2.36 (t, $J = 7.32$ Hz, 4H), 4.08–4.14 (t, $J = 6.73$ Hz, 4H) and 5.38–5.42 ppm (m, 2H); ^{13}C NMR δ 25.5, 26.3, 27.4, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.8, 34.8, 64.6, 130.1 (*cis*, 20%), 130.6 (*trans*, 80%) and 174.3 ppm. Anal. Calcd for $C_{36}H_{66}O_4$: C, 76.87; H, 11.74. Found: C, 77.08; H, 12.03%.

4.4. Polymerization of monomers **5**, **6** and **8–14** by ADMET

The following polymerization is typical. The results are summarized in Table 1.

4.4.1. Polymer **18** from monomer **5**

Monomer **5** (8.00 g, 23.8 mmol) was placed in a round-bottomed flask (100 mL). This was connected to a vacuum (0.1 mm of Hg) and the monomer degassed for 30 min with vigorous stirring. The vacuum was then broken and argon gas was passed into the flask for a further 15 min. Catalyst **1** (196.0 mg, 0.24 mmol, 1 mol%) was added and the vacuum re-applied. The reaction mixture effervesced as ethene evolved. The mixture was left to stir at 25 °C under vacuum for 24 h. The viscous product so obtained was dissolved in a small amount of dichloromethane at 25 °C and treated with a fresh portion (1 mol%) of catalyst **1** for a further 24 h. The solid mass that formed was re-dissolved in $CHCl_3$ (25 mL) and precipitated into MeOH (500 mL). The final polymer was a pale grey solid (6.32 g, 86%). It had $T_m = 57$ °C; M_n 5400, M_w 9300, M_w/M_n 1.7; IR (cast film) 1732 cm^{-1}; ^1H NMR δ 1.20–1.40 (bs, 22H), 1.56–1.70 (m, 4H), 1.94–2.10 (m, 4H), 2.30 (t, $J = 7.69$ Hz, 2H), 4.10 (t, $J = 6.72$ Hz, 2H) and 5.30–5.50 ppm (m, 2H), very small end-group peaks appeared at 4.92–5.08 and 5.76–5.90 ppm; ^{13}C NMR δ 24.9, 25.9, 27.1, 28.6, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5 29.6 29.7, 32.5, 33.7, 34.3, 64.3, 114.0, 129.8 (*cis*, 18%), 130.2 (*trans*, 82%) and 173.9 ppm.

The following polymers were prepared using a similar procedure. The molecular weights are given in Table 1.

4.4.2. Polymer **19** from monomer **6**

This polymer (90% yield) was obtained as a grey powder. It had $T_m = 59$ °C; IR (cast film) 1734 cm^{-1}; ^1H NMR δ 1.20–1.46 (m, 24H), 1.58–1.72 (m, 8H), 1.95–2.05 (m, 4H), 2.28–2.36 (t, $J = 7.55$ Hz, 4H), 4.05–4.15 (t, $J = 6.73$ Hz, 4H) and 5.36–5.43 ppm (m, 2H), very small end-group peaks appeared at 5.00 and 5.85 ppm; ^{13}C NMR δ 24.9, 25.5, 27.1, 28.5, 29.0, 29.1, 29.2, 29.3, 29.6, 29.7 32.5, 34.3, 64.0, 129.8 (*cis*, 18%), 130.2 (*trans*, 82%) and 173.8 ppm.

4.4.3. Polymer **20** from monomer **8**

This polymer (78%) was obtained as a waxy solid. It had IR (cast film) 1733 cm^{-1}; ^1H NMR δ 1.34 (bs, 30H), 1.68 (m, 10H), 2.32 (t, $J = 7.42$ Hz, 4H), 4.09 (t, $J = 6.73$ Hz, 4H) and 5.40 ppm (m, 2H), very small end-group peaks appeared at 5.00 and 5.85 ppm; ^{13}C NMR δ 24.7, 25.6, 26.9, 28.3, 28.8, 28.9, 29.0, 29.1, 29.3, 29.4, 32.3, 34.1, 64.1, 129.6 (*cis*, 18%), 130.0 (*trans*, 82%) and 173.7 ppm.

4.4.4. Polymer **21** from monomer **9**

This polymer (57%) was obtained as a sticky gum. It had $T_g = -36$ °C and $T_m = 52$ °C; IR (cast film) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28–2.44 (m, 4H), 2.66 (s, 4H), 4.00–4.14 (t, $J = 6.81$ Hz, 4H) and 5.46–5.52 ppm (m, 2H), there were small end-group peaks appearing at 5.06–5.18 and 5.74–5.88 ppm; ^{13}C NMR δ 27.1, 29.3, 32.6, 63.9, 64.1, 127.7 (*cis*, 30%), 128.5 (*trans*, 70%), 172.4 and 172.5 ppm.

4.4.5. Polymer **22** from monomer **10**

This polymer was obtained (70%) as a white powder. It had IR (cast film) 1735 cm^{-1}; ^1H NMR δ 1.20–1.40 (m, 24H), 1.60–1.70 (m, 4H), 1.92–2.10 (m, 4H), 2.60 (s, 4H), 4.02–4.12 (t, $J = 6.73$ Hz, 4H) and 5.35–5.45 ppm (m, 2H), small olefinic end-group peaks appeared at 4.90–5.05 and 5.75–5.90 ppm.

4.4.6. Polymer **23** from monomer **11**

This polymer was obtained (91%) as a gum. It had $T_m = 58\ ^\circ C$; IR (cast film) 1735 cm^{-1}; ^1H NMR δ 1.20–1.40 (m, 24H), 1.60–1.80 (m, 8H), 1.92–2.10 (m, 4H), 2.30–2.40 (m, 4H), 4.02–4.12 (t, $J = 6.73$ Hz, 4H) and 5.35–5.45 ppm (m, 2H), small olefinic end-group peaks appeared at 4.90–5.05 and 5.75–5.90 ppm; ^{13}C NMR δ 24.5, 25.8, 27.1, 28.5, 28.8, 28.9, 29.0, 29.2, 29.4, 29.6, 29.7, 32.5, 33.7, 33.9, 64.5, 129.8 (*cis*, 18%), 130.2 (*trans*, 82%) and 173.0 ppm (C=O).

4.4.7. Polymer **24** from monomer **12**

This polymer (88%) was obtained as a waxy solid. It had IR (cast film) 1734 cm^{-1}; ^1H NMR δ 1.29 (bs, 36H), 1.65 (m, 8H), 2.00 (m, 4H), 2.32 (t, $J = 7.41$ Hz, 4H), 4.09 (t, $J = 6.73$ Hz, 4H) and 5.42 ppm (m, 2H), very small end-group peaks appeared at 5.00 and 5.85 ppm; ^{13}C NMR δ 24.9, 25.9, 28.6, 29.1, 29.2, 29.3, 29.4, 29.6, 32.5, 34.3, 64.3, 120.8 (*cis*, 19%), 130.2 (*trans*, 81%) and 173.9 ppm.

4.4.8. Polymer **25** from monomer **13**

This polymer (92%) was obtained as a sticky gum. It had $T_g = -16\ ^\circ C$, $T_m = 85\ ^\circ C$; IR (cast film) 1720 cm^{-1}; ^1H NMR δ 1.80–1.92 (m, 4H), 2.10–2.26 (m, 4H), 4.28–4.42 (t, $J = 6.32$ Hz, 4H), 5.40–5.60 (m, 2H), 7.55 (t, $J = 7.69$ Hz, 1H), 8.14–8.28 (m, 2H) and 8.68 ppm (s, 1H), small end-group peaks appearing at 4.90–5.05 and 5.75–5.90 ppm; ^{13}C NMR δ 23.52, 28.3, 28.4, 28.8, 64.6, 129.3 (*cis*, 15%), 129.8 (*trans*, 85%), 130.5, 130.8, 133.5 and 165.6 ppm.

4.4.9. Polymer **26** from monomer **14**

This polymer (48%) was obtained as a grey powder. It had $T_g = -40\ ^\circ C$ and $T_m = 59\ ^\circ C$; IR (cast film) 1745 cm^{-1}; ^1H NMR δ 2.30–2.50 (m, 4H), 4.10–4.20 (t, $J = 6.74$ Hz, 4H) and 5.45–5.60 ppm (m, 2H), end-group peaks were not detected; ^{13}C NMR δ 32.2, 67.2, 67.4, 127.5 (*cis*, 28%), 128.4 (*trans*, 72%) and 155.4 ppm.

4.5. Synthesis of polymer **18** using phase transfer catalysis

(a) *Self-metathesis of methyl undec-10-enoate*: neat methyl undec-10-enoate (2.00 g, 10.0 mmol) was purged with argon for 10 min then stirred with catalyst **1** (4.16 mg, 0.5 mol%) at 20 °C under an argon atmosphere for 18 h. The product was recrystallized twice from petroleum ether (60:80). This gave a mixture of the dimethyl esters of diacid **27** (1.23 g, 33%) as a pale brown gum. It had IR (cast film) 1739 cm^{-1}; ^1H NMR δ 1.31 (m, 24H), 1.64 (m, 4H), 2.00 (m, 2H), 3.70 (s, 6H) and 5.41 ppm (m, 2H). ^{13}C NMR δ 24.9, 28.9, 29.0, 29.1, 29.5, 32.5, 34.0, 51.4, 128.2 (*cis*, 20%), 130.2 (*trans*, 80%) and 174.3 ppm. Anal. Calcd for $C_{22}H_{40}O_4$: C, 71.74; H, 10.87. Found: C, 71.76; H, 11.26%.

(b) *Diacid **27***: the dimethyl ester prepared above (1.0 g, 2.7 mmol) was heated with a mixture of sodium hydroxide (0.24 g), methanol (10 mL) and water (2 mL) under reflux for 2 h. On cooling the sodium salt of the acid precipitated. It was filtered off, dissolved in water and the solution acidified with hydrochloric acid. The precipitated acid was filtered off, washed with water and dried. The diacid **27** (0.37 g, 40%) was obtained as a white solid, m.p. 42–50 °C. It had IR (cast film) 1693 cm^{-1}; ^1H NMR δ 1.30 (m, 20H), 1.60 (m, 4H), 2.00 (m, 4H), 2.30 (t, $J = 7.26$ Hz) and 5.40 ppm (m, 2H). ^{13}C NMR δ 24.6, 28.6, 28.7, 28.9, 29.2, 32.1, 33.5, 128.0 (*cis*, 20%), 130.0 (*trans*, 80%) and 174.3 ppm. Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.59; H, 10.59. Found: C, 70.87; H, 10.79%.

(c) *Dibromide **28***: neat undec-10-enyl bromide (8.00 g, 34.2 mmol) was purged with argon for 10 min then stirred with catalyst **1** (7.06 mg, 0.5 mol%) at 20 °C under an argon atmosphere for 18 h. Short path fractional distillation removed unreacted starting material. The residue was purified by passage through a short alumina column in hexane. This gave dibromide **28** as a viscous pale yellow oil (6.30 g, 84%). It had IR (cast film) 1730 cm^{-1}; ^1H NMR δ 1.32 (m, 24H), 1.88 (m, 4H), 2.00 (m, 4H), 3.44 (t, $J = 6.87$ Hz) and 5.40 ppm (m, 2H). ^{13}C NMR δ 28.1, 28.7, 29.0, 29.2, 29.3, 29.5, 29.7, 32.8, 34.0, 129.8 (*cis*, 20%) and 130.3 ppm (*trans*, 80%). Anal. Calcd for $C_{20}H_{38}Br_2$: C, 54.79; H, 8.67; Br, 36.54. Found: C, 55.00; H, 8.79; Br, 36.74%.

(d) *Synthesis of polymer **18***: diacid **27** (1.00 g, 2.94 mmol), dibromide **28** (1.29 g, 2.94 mmol), tetra-*n*-butylammonium hydroxide (2.10 g, 3.24 mmol, as a 40% solution in water) and chloroform were reacted together and the product isolated using the general procedures described in detail previously [37]. This gave polymer **18** (1.64 g, 80%). It had spectra the same as those reported above and M_n 8200 and M_w 14,700.

4.6. Synthesis of polymer **19** using phase transfer catalysis

Diacid **27** (1.00 g, 2.94 mmol), 1,6-dibromohexane (0.72 g, 2.94 mmol), tetra-*n*-butylammonium hydroxide (2.10 g, 3.24 mmol, as a 40% solution in water) and chloroform were reacted together and the product isolated using the procedures described in detail previously [37]. This gave polymer **19** (0.62 g, 51%). It had spectra the same as those reported above and M_n 4100 and M_w 6300.

4.7. Synthesis of polymer **24** using phase transfer catalysis

1,10-Decanedicarboxylic acid (0.68 g, 2.94 mmol), dibromide **28** (1.29 g, 2.94 mmol), tetra-*n*-butylammonium hydroxide (2.10 g, 3.24 mmol, as a 40% solution in water) and chloroform were reacted together and the product isolated using the procedures described in detail previously [37]. This gave polymer **24** (1.10 g, 74%). It had spectra the same as those reported above and M_n 6900 and M_w 13,100.

4.8. Cyclo-depolymerizations using catalyst **1**

The following CDP, summarized in Table 3 entry 2, is typical. The results of the other CDPs are also summarized in Table 3.

4.8.1. CDP of poly(1,6-hexanyl bis(undec-10-enoate)) (**19**)

Poly(1,6-hexanyl bis(undec-10-enoate)) (**19**) (2.50 g, 5.95 mmol) was dissolved in dichloromethane (250 mL) which had been purged with argon for 1 h prior to use. Grubbs' catalyst **1** (49 mg, 5.95 mmol, 1 mol% based on polymer repeat unit) was then added and the mixture stirred gently at 23 °C under a positive pressure of argon. The progress of the reaction was monitored by GPC. Analysis showed that about 70% of the polymer had reacted by the 4th day and there was no further change by the 6th day. A further 1 mol% of Grubbs' catalyst **1** was added and the reaction was allowed to proceed for a further 3 days until equilibrium was attained. The reaction was stopped and the solvent evaporated to give the crude product (2.46 g). The crude mixture was passed through a short alumina column using dichloromethane as solvent. This afforded an off-white waxy solid consisting of MCOs **30** (1.79 g, 73%). The MCOs had IR (cast film) 1734 cm^{-1}; ^{1}H NMR δ 1.20–1.50 (m, 24H), 1.58–1.74 (m, 8H), 1.94–2.10 (m, 4H), 2.26–2.36 (m, 4H), 4.00–4.20 (m, 4H) and 5.35–5.45 ppm (m, 2H), there were no peaks attributable to vinyl end groups; ^{13}C NMR δ 24.9, 25.6, 26.9, 27.1, 28.4, 28.5, 28.8, 28.9, 29.0, 29.2, 29.4, 32.2, 32.4, 34.3 34.4, 63.9, 64.0, 129.9, 130.2, 130.4 and 173.0 ppm. The MALDI-ToF mass spectrum of the product showed mass peaks corresponding to from the cyclic monomer (446, monomer + Na$^+$) up to the cyclic pentamer (2136, pentamer + Na$^+$), see Fig. 2a. The percentage distribution of the cyclics is given in Table 3 entry 2, while the GPC trace is shown in Fig. 1a. Percentage ratio of the geometrical isomers: 21% *Z*, 79% *E*.

The following CDPs using catalyst **1** were carried out similarly.

4.8.2. CDP of polymer **20**

This gave MCOs **31** (59%). They had IR (cast film) 1736 cm^{-1}; ^{1}H NMR (cast film) δ 1.20–1.40 (bs, 32H), 1.58–1.74 (m, 8H), 1.94–2.10 (m, 4H), 2.28–2.38 (m, 4H), 4.00–4.18 (t, $J = 7.01$ Hz, 4H) and 5.35–5.45 ppm (m, 2H), there were no peaks attributable to any end groups; ^{13}C NMR δ 25.3, 26.2, 27.4, 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.6, 34.7, 34.8, 64.6, 129.9, 130.2, 130.7 and 174.3 ppm. The MALDI-ToF mass spectrum of the product showed a series of mass peaks corresponding to from the cyclic monomer (503, monomer + Na$^+$) up to the cyclic hexamer (2894, hexamer + Na$^+$). The percentage distribution of the cyclic species is given in Table 3 entry 4.

4.8.3. CDP of polymer **23**

This CDP gave MCOs **34** (96%) as a white waxy solid. They had IR (cast film) 1736 cm^{-1}; ^{1}H NMR δ 1.20–1.40 (m, 24H), 1.56–1.760 (m, 8H), 1.94–2.10 (m, 4H), 2.30–2.40 (m, 4H), 4.02–4.16 (m, 4H) and 5.35–5.45 ppm (m, 2H), there were no end-group peak visible on the spectrum; ^{13}C NMR δ 24.4, 25.8, 25.9, 27.1, 28.1, 28.4, 28.5, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5, 32.2, 32.5, 33.8, 33.9, 64.5, 129.8, 129.9, 130.23, 130.4 and 173.3 ppm. The MALDI-ToF mass spectrum of the product showed a series of mass peaks corresponding to from the cyclic monomer (445, monomer + Na$^+$) up to the cyclic hexamer (2558, hexamer + Na$^+$). GPC showed a series of MCOs peaks with the size of the peaks decreasing as the oligomer size became larger. The percentage distribution of the cyclics species is given in Table 3 entry 8. Percentage ratio of the isomers: 18% *cis*, 82% *trans*.

4.8.4. CDP of polymer **24**

This gave MCOs **35** (74%) as an off-white solid. They had IR (cast film) 1735 cm^{-1}; ^{1}H NMR δ 1.20–1.44 (bs, 36H), 1.56–1.72 (m, 8H), 1.94–2.10 (m, 4H), 2.28–2.38 (m, 4H), 4.02–4.18 (m, 4H) and 5.35–5.45 ppm (m, 2H), there were no end-group peak visible on the spectrum; ^{13}C NMR δ 25.3, 26.1, 26.2, 27.4, 28.8, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 32.7, 32.9, 34.7, 34.8, 64.6, 64.7, 130.2, 130.6, 130.7 and 174.2 ppm. The MALDI-ToF mass spectrum of the product showed a series of mass peaks corresponding to from the cyclic monomer (531, monomer + Na$^+$) up to the cyclic pentamer (2553, pentamer + Na$^+$); GPC showed a progression of peaks with the size of decreasing as the oligomer size became larger. The percentage distribution of the cyclics species is given in Table 3 entry 9.

4.8.5. CDP of polymer **25**

This gave MCOs **36** (57%) as a white powder. They had IR (cast film) 1719 cm^{-1}; ^{1}H NMR δ 1.80–1.92 (m, 4H), 2.10–2.30 (m, 4H), 4.26–4.46 (m, 4H), 5.48–5.60 (m, 2H), 7.48–7.60 (m, 1H), 8.15–8.30 (m, 2H) and 8.65–8.70 ppm (m, 1H), there were no peaks attributable to vinyl end groups; ^{13}C NMR δ 23.6, 23.8, 28.2, 28.3, 28.4, 28.9, 29.2, 29.5, 64.3, 64.4, 64.6, 128.5 128.6, 128.8, 129.3, 129.5 129.8, 130.2, 130.3, 130.4, 130.6, 130.7, 132.1, 133.1, 133.3, 133.5, 133.6, 133.7, 155.5, 165.6 and 165.7 ppm. The MALDI-ToF mass spectrum of the product showed a series of mass peaks corresponding to from the cyclic dimer (572, dimer + Na$^+$) up to the cyclic hexamer (1669, hexamer + Na$^+$). There were a few peaks of lower intensity attributable to linear oligomers. GPC (oligomer column) showed a progression of peaks with the size of the peaks decreasing as the oligomer size became larger. The percentage distribution of the cyclics species is given in Table 3 entry 11.

4.9. Cyclo-depolymerizations using catalyst **2**

The following CDP, summarized in Table 3 entry 5, is typical. The results of the other CDPs are also summarized in Table 3.

4.9.1. CDP of polymer **20**

The CDP of polymer **20** (1.00 g, 2.91 mmol) was carried out using the same procedure as above but using the "second generation" Grubbs' catalyst **2** (18 mg) and dichloromethane

(100 mL). The reaction mixture was heated to 40 °C and monitored by GPC. Within 2 h the reaction was complete. The crude reaction mixture was passed through a short alumina column using DCM as eluant to yield grey waxy MCOs **31** (0.52 g, 52%). Their spectroscopic and analytical data were essentially the same as given above. The percentage distribution of the cyclic species is given in Table 3 entry 5.

The following CDPs using catalyst **2** were carried out similarly.

4.9.2. CDP of polymer **18**

This gave MCOs **29** (51%) as a cream colored wax. They had IR (cast film) 1736 cm^{-1}; ^{1}H NMR δ 1.20–1.40 (bs, 22H), 1.56–1.70 (m, 4H), 1.94–2.10 (m, 4H), 2.28–2.40 (m, 2H), 4.05–4.20 (m, 2H) and 5.30–5.50 ppm (m, 2H), there were no signals due to vinyl groups; ^{13}C NMR δ 24.9, 25.9, 27.1, 28.6, 28.8, 29.0, 29.2, 29.3, 29.4, 29.5 29.6 29.7, 32.5, 33.7, 34.3, 64.3, 114.0, 129.8, 130.2 and 173.9 ppm. The MALDI-ToF mass spectrum of the product showed mass peaks corresponding to the cyclic dimer (640, dimer + Na^+) and the trimer (948, trimer + Na^+). The percentage distribution of the cyclic species is given in Table 3 entry 1.

4.9.3. CDP of polymer **19**

This gave MCOs **30** (84%) as a white wax. The MALDI-ToF MS is shown in Fig. 2b. Other analytical data were essentially the same as that given above: see Table 3 entry 3.

4.9.4. CDP of polymer **21**

This gave MCOs **32** (92%) as a white wax. They had IR (cast film) 1730 cm^{-1}; ^{1}H NMR δ 2.28–2.44 (m, 4H), 2.59 (s, 4H), 4.06–4.28 (t, $J = 6.81$ Hz, 4H) and 5.44–5.52 ppm (m, 2H); there were no peaks attributable to end groups; ^{13}C NMR δ 27.2, 29.6, 30.4, 30.6, 32.2, 33.5, 62.1, 63.4, 128.6, 128.9, 129.6, 172.8, 172.1 and 172.2 ppm. The MALDI-ToF mass spectrum of the product showed mass peaks corresponding to from the cyclic dimer (419, dimer + Na^+) up to the cyclic tetramer (814, tetramer + Na^+). The percentage distribution of the cyclic species is given in Table 3 entry 6.

4.9.5. CDP of polymer **22**

This gave MCOs **33** (80%) as a pale brown oil. They had IR (cast film) 1740 cm^{-1}; ^{1}H NMR δ 1.20–1.40 (m, 24H), 1.50–1.70 (m, 4H), 1.90–2.10 (m, 4H), 2.30–2.45 (s, 4H), 4.00–4.20 (t, $J = 6.73$ Hz, 4H) and 5.30–5.69 ppm (m, 2H), there were no peaks attributable to end groups. The MALDI-ToF mass spectrum of the product showed mass peaks corresponding to from the cyclic monomer (417, monomer + Na^+) up to the cyclic tetramer (1599, tetramer + Na^+). The percentage distribution of the cyclic species is given in Table 3 entry 7.

4.9.6. CDP of polymer **24**

This gave MCOs **35** (95%) as an off-white solid. Their spectroscopic and analytical data were essentially the same as given above. The percentage distribution of the cyclic species is given in Table 3 entry 10.

4.9.7. CDP of polymer **26**

This gave MCOs **37** (97%) as a waxy solid. They had IR (cast film) 1736 cm^{-1}; ^{1}H NMR δ 2.34–2.48 (m, 4H), 4.08–4.28 (m, 4H) and 5.50–5.60 ppm (m, 2H): there were no peaks attributable to end groups; ^{13}C NMR δ 31.9, 32.2, 67.0, 67.2, 67.3, 67.4, 127.8, 128.8, 128.4, 128.6, 129, 129.1, 155.4 and 155.6 ppm. The MALDI-ToF mass spectrum of the product showed a series of mass peaks corresponding to from the cyclic dimer (307, dimer + Na^+) up to the cyclic hexamer (876, hexamer + Na^+). The percentage distribution of the cyclics species is given in Table 3 entry 12.

4.10. CDPs by transesterification

4.10.1. CDP of polymer **18** catalysed by di-n-butyltin oxide

A mixture of polymer **18** (835 mg, 2.71 mmol) and di-*n*-butyltin oxide (13.5 mg, 0.054 mmol, 2 mol%) were dissolved in 1,2-dichlorobenzene (35 mL) and the mixture was heated under reflux. The reaction was monitored by GPC analysis and the reaction continued until the yield was satisfactory. After 9 days the MCOs **29** were isolated using the procedure described previously [43], and were characterized as above. The results are summarized in Table 3 entry 13.

4.10.2. CDP of polymer **18** catalysed by di-n-butoxydi-n-butyltin **38**

This experiment was similar to the preceding one but using di-*n*-butoxydi-*n*-butyltin (**38**) as the catalyst, chlorobenzene as the solvent, a reflux temperature of *ca.* 133 °C and a reaction time of 10 h. The results are summarized in Table 3 entry 14.

4.11. Entropically-driven ring-opening metathesis polymerization of olefin-containing MCOs

Two different procedures were used. The first, which was used in all except two cases, involved carrying out the reaction in a glass tube or flask. The second involved carrying out the reaction with the reactants as a film. The results are summarized in Table 5.

4.11.1. ED-ROMP of MCOs **30**: entry 6 in Table 5

In a round-bottom flask (5 mL) equipped with a small magnetic stirrer bar MCOs **30** (103.0 mg, 0.244 mmol), prepared the experiment summarized in Table 3 entry 3, were dissolved in dichloromethane (0.25 mL) which had been purged with argon for 1 h prior to use. Catalyst **1** (2.0 mg, 2.44×10^{-3} mmol, 1 mol%) was then added and the reaction mixture stirred at 25 °C under a positive pressure of argon. The polymerization was monitored by GPC (see text for details). After 3 h all the dichloromethane had evaporated with the argon stream. The mixture was allowed to stand for another 8 h. The product was dried under vacuum to afford a hard polymer. A sample was analyzed by GPC. The results are summarized in Table 5.

4.11.2. ED-ROMP of lactone **7***: entry 4 in Table 5*

Lactone **7** (50.0 mg, 8.90×10^{-2} mmol) and catalyst **2** (0.8 mg, 8.90×10^{-4} mmol) were dissolved in chloroform (1.0 mL). The solution was quickly applied onto a microscope slide and placed in a Buchi vacuum oven maintained at 40 °C. The chloroform quickly evaporated to leave a film. After 15 min a polymeric film had formed. The slide was removed from the oven and allowed to cool to 20 °C. A sample of the final film was removed and analyzed by GPC. The results are summarized in Table 5.

4.12. Reprecipitation

A portion of the reaction product (*ca.* 80 mg) was dissolved in a minimum amount of chloroform (0.1 mL) and precipitated into methanol (2.0 mL). The polymer was allowed to settle then methanol was carefully decanted off. The precipitate was washed with cold (0 °C) methanol and dried overnight in a vacuum oven at 25 °C and 0.1 mm Hg to give a white powdery polymer (*ca.* 70 mg). It was characterized by GPC, ^{1}H and ^{13}C NMR spectroscopies. The results are summarized in Table 6.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.09.014.

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