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Cyclo-depolymerisation of polyundecanoate and related polyesters: characterisation of cyclic oligoundecanoates and related cyclic oligoesters

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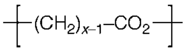
The cyclo-depolymerisation of linear polyundecanoate has been studied in detail. The cyclic oligomers produced were characterised by gel permeation chromatography, ^{1}H NMR spectroscopy and mass spectroscopy in comparison with the corresponding linear oligomers. A sample of the cyclic dimer was isolated and its crystal structure determined. Cyclic oligooctanoates, oligodecanoates and oligododecanoates were prepared similarly. The ring-opening polymerisation of the cyclic oligoundecanoates was briefly investigated.

Introduction

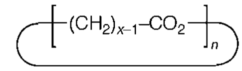
For statistical reasons[1–3] the products of step-growth polymerisations generally contain a small cyclic oligomer fraction, typically $<2\%$ of the mass. As a consequence a wide range of cyclic oligomers has been known for many years.[4–6] The presence of the cyclic oligomers can adversely affect the properties of the polymeric product. For example, they may modify the mechanical properties of the product by plasticising it. It has, however, been recognised in recent years that cyclic oligomers can also have useful properties. Thus, if they are freely available in quantity they may serve as starting materials for novel entropically-driven ring-opening polymerisations (ED-ROP),[7–9] or they may serve as useful building blocks for various interesting types of polymer structures,[10] especially if they have reactive functional groups.[11] These possibilities have prompted a keen and increasing interest in the synthesis and properties of cyclic oligomers.[12] Three main types of synthetic approach have been investigated. In the first type cyclic oligomers have been synthesised directly from monomers under high-dilution conditions.[13–19] In the second type they have been synthesised from high-molecular-weight linear polymers by cyclo-depolymerisation (CDP).[20–27] The third type involves the cyclo-oligomerisation of polymer-supported monomers, procedures which facilitate isolation of the cyclic products.[28–33]

The CDP approach to the synthesis of cyclic oligomers uses the corresponding linear polymers as the starting materials. Reaction conditions for CDP are chosen so that the linkages joining the polymer repeat units are repeatedly broken and then re-formed. There is then an equilibration process and if this is achieved at high dilution the effect is similar to that of carrying out a synthesis at high dilution and cyclic oligomers are obtained in good yield. Whilst such ring–chain equilibria are very well known,[1,2,34] it has perhaps not been fully appreciated until recently that the high dilution requirement is not too limiting and good yields of cyclic oligomers can often be obtained in practically significant quantities using approximately 2% w/v solutions. Various families of cyclic oligoesters have already been synthesised by CDP including polycaprolactone,[20] poly(ethylene terephthalate),[21,22] poly(butylene terephthalate),[21,24,25] poly(decamethylene terephthalate),[35] poly(tetraethylene glycol terephthalate),[36] poly(hexamethylene succinate),[26] poly(tetraethylene glycol succinate)[37] and a wide range of poly(alkylene isophthalate)s.[23]

This paper describes the CDP of polyundecanoate (**1**), a readily accessible linear polymer, and the characterisation of the cyclic oligoundecanoates (**2**) so obtained. Our objective was to characterise the cyclic oligomers using a range of analytical methods so that they could be identified easily in other studies. Cyclic oligoundecanoates (**2**) are attractive preliminary targets to test many potential methods for the synthesis of cyclic oligomers because they, and the corresponding linear poly- and oligo-undecanoates, are readily soluble in a wide range of organic solvents. For similar reasons cyclic oligooctanoates (**3**), cyclic oligodecanoates (**4**) and cyclic oligododecanoates (**5**) were also prepared and characterised. Spanagel and Carothers have previously described the CDP of polydecanoate (**6**), polytridecanoate (**7**) and polytetradecanoate (**8**) by heating them under vacuum at 270 °C in the presence of magnesium chloride and collecting the distillate.[38] Under these conditions the potential equilibria were displaced by continuously removing the more volatile small cyclics. The main products in the distillates were, respectively, the cyclic dimer, the cyclic dimer and the cyclic monomer. The cyclic oligoundecanoates (**2**) have been synthesised previously using a polymer-supported method.[30,32,33]


$-\!\!\left[(CH_2)_{x-1}-CO_2\right]\!\!-$

1 $x = 11$
6 $x = 10$
7 $x = 13$
8 $x = 14$
15 $x = 8$
16 $x = 12$


$\left[(CH_2)_{x-1}-CO_2\right]_n$

2 $x = 11$
3 $x = 8$
4 $x = 10$
5 $x = 12$

Results and discussion

Synthesis and characterisation of cyclic oligoundecanoates (2)

Polyundecanoate (**1**) was prepared by vigorously stirring a solution of commercial 11-bromoundecanoic acid in chlorobenzene at *ca.* 100 °C with an equimolar amount of aqueous tetra-*n*-butylammonium hydroxide solution for 36 h.[39] This gave polyundecanoate (**1**) with M_n 23 200 and M_w 41 600. Cyclo-depolymerisation of this product was successfully achieved using dibutoxydibutyltin (**9**)[21] as the catalyst. Thus, heating a 2% w/v solution of the polymer with 2 mol% of this catalyst in chlorobenzene at reflux temperature (*ca.* 133 °C) for 8 h gave the cyclic oligomers (**2**) in 90% yield. The reaction was conveniently monitored by gel permeation chromatography (GPC): see Fig. 1. Similar experiments (not described here in

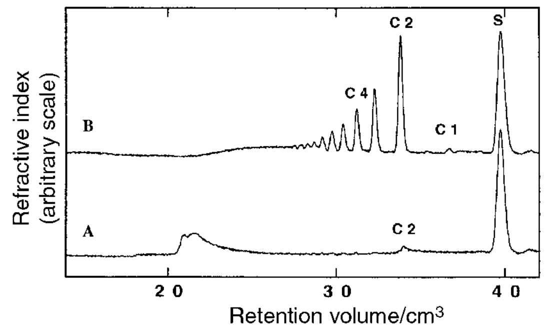
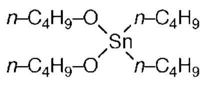


Fig. 1 GPC traces of starting polyundecanoate (**1**) (trace A) and the cyclic oligoundecanoates (**2**) (trace B) obtained by the CDP. S indicates a toluene marker peak.

detail) indicated that high yields of cyclics were only obtained if the concentration of the solution was ⩽3% w/v and the reaction time was at least 6 h.



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$Br\left[(CH_2)_{10}\text{–}CO_2\right]_nH$

10

The cyclic oligoundecanoates (**2**) were characterised using various methods. To assist in the characterisation linear oligoundecanoates (**10**), average degree of polymerisation (DP_n) 3.4, were prepared by repeating the synthesis of the linear polymer, but using chloroform as the reaction solvent at *ca.* 61 °C with a reaction time of only 6 h. The ^1H NMR spectrum of the linear oligomers showed a signal due to $\text{–}CO_2CH_2\text{–}$ at δ 4.07 ppm and a signal due to the $BrCH_2\text{–}$ end groups at δ 3.39 ppm. The spectrum of the cyclic oligomers showed a strong signal at δ 4.07 ppm but only a very weak signal, corresponding to a DP_n of 60, at δ 3.39 ppm. Given the results of the GPC analysis discussed below, this indicates that >94% of the oligomer molecules are cyclic. The FT-IR spectrum of the linear oligomers showed a strong ester carbonyl band at 1727 cm^{-1} with a shoulder at 1708 cm^{-1} due to the acid end groups. The spectrum of the cyclic oligomers showed just a sharp ester band at 1729 cm^{-1}.

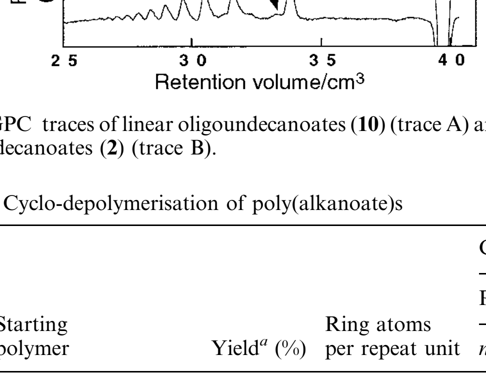


Fig. 2 GPC traces of linear oligoundecanoates (**10**) (trace A) and cyclic oligoundecanoates (**2**) (trace B).

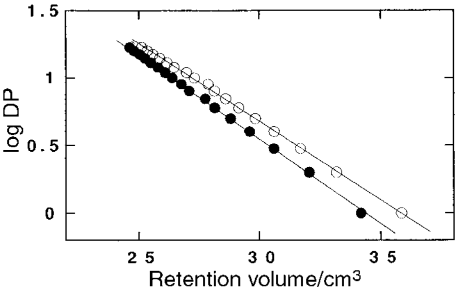
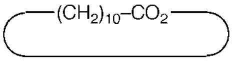


Fig. 3 Plots of 'log DP' *versus* 'Retention Volume' for linear (●) and cyclic (○) oligoundecanoates.

The most detailed analysis of the cyclic oligomers was achieved by GPC. As expected, the smaller linear and cyclic oligomers had significantly different retention volumes on the GPC trace, see Fig. 2, and so they could easily be distinguished. Plots of 'log DP_n' *versus* 'Retention Volume' for the two series, shown in Fig. 3, are essentially straight lines. The CDP product proved to consist almost entirely of cyclic oligomers and the DP_n was 3.51. The amount of each cyclic present was as summarised in Table 1. Not surprisingly, since it is a strained 'medium-sized' ring,[40] the cyclic monomer, *i.e.* undecanolactone (**11**), formed less than 2% of the cyclic fraction. The main component, 56% by weight, was the cyclic dimer (**12**) and, as expected from the theory of Jacobson and Stockmeyer,[41] the larger oligomers were then present in amounts which decreased progressively as the rings became larger. Under the best GPC conditions cyclic oligomers up to the 18-mer (216 ring atoms) were detected.



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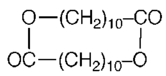

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The MALDI-ToF mass spectrum of the cyclic product (doped with K^+ cations in the form of KBr) confirmed the presence of rings from the cyclic trimer up to the cyclic 14-mer: see Fig. 4a. For each cyclic there was a strong $[M+K]^+$ peak and a weaker $[M+Na]^+$ peak. For the cyclic hexamer, for example, these peaks appeared at masses 1144 (calculated: 1144) and 1128 (1128). The spectrum of the linear oligomers confirmed that linears with Br– and $\text{–}CO_2H$ end groups were present from the trimer up to the 17-mer: see Fig. 4b. Thus, the peaks appeared at the expected $[M+K]^+$ positions and as doublets due to bromine having isotopes of 79 and 81 in

Table 1 Cyclo-depolymerisation of poly(alkanoate)s

				Composition of product[a]									
				Percentage yields of cyclic *n*-mers by weight									
Entry	Starting polymer	Yield[a] (%)	Ring atoms per repeat unit	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=>8$[b]	MALDI-ToF MS[c]
1	Polyundecanoate (**1**)	90	12	1.7	56[d]	22	8.0	4.0	3.0	1.8	1.2	1.3	14
2	Polyoctanoate (**15**)	82	9	<0.1	76	16	4.5	1.3	0.5	0.2	0.1	1.4	8
3	Polydecanoate (**6**)	87	11	1.0	80	14	3.1	0.7	0.3	0.2	0.1	0.5	10
4	Polydodecanoate (**16**)	81	13	1.7	73	18	4.2	1.5	0.5	0.2	0.1	0.8	7

[a] By GPC analysis. [b] These values are mainly due to unidentified higher cyclic oligomers. [c] Samples of products were studied by MALDI-ToF mass spectrometry. Peaks due to cyclics were clearly seen from $n=3$ up to the values given. [d] A pure sample of this cyclic dimer was isolated.

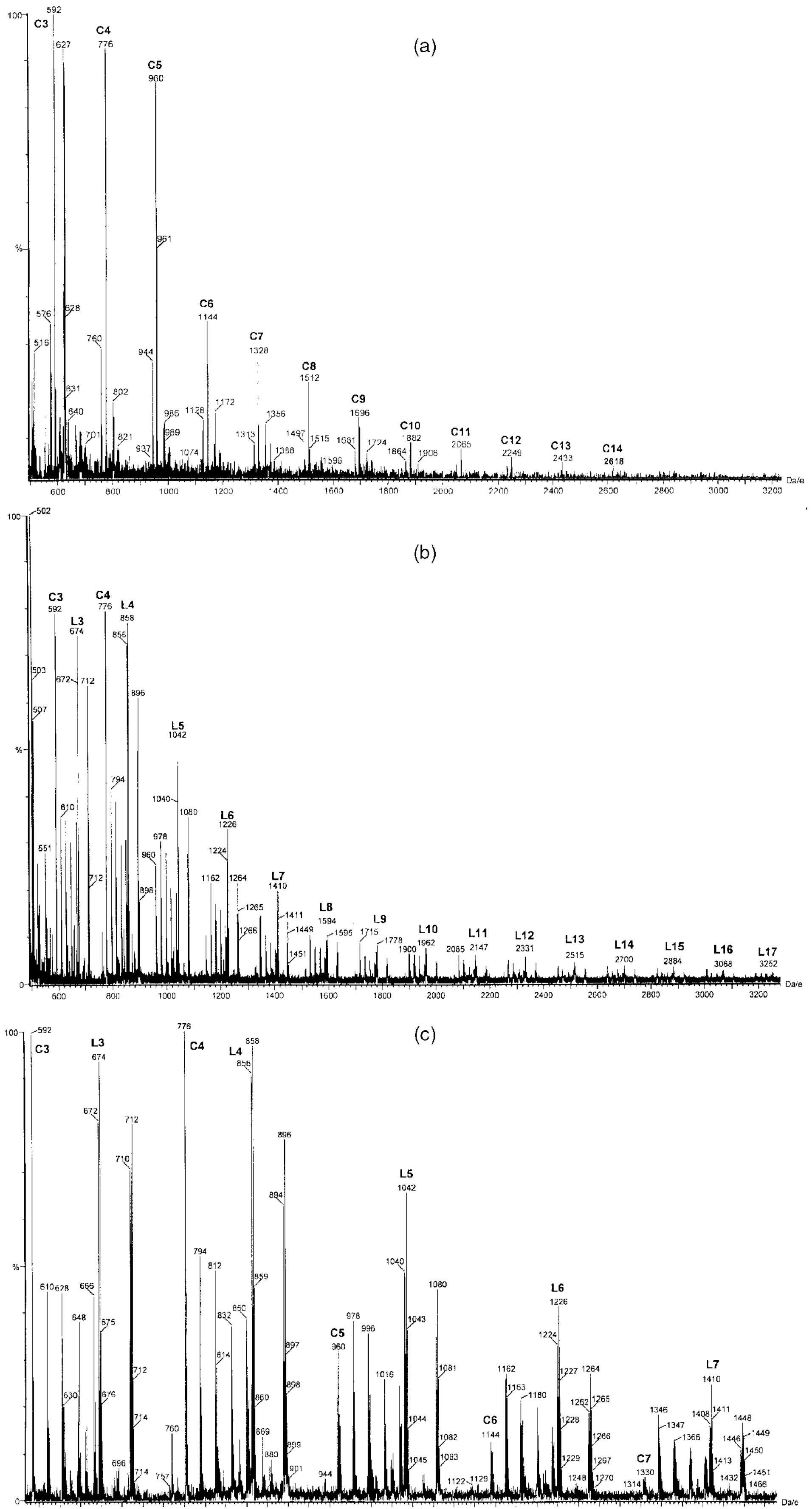


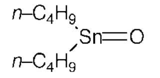
Fig. 4 MALDI-ToF mass spectra for samples of (a) cyclic oligoundecanoates (**2**), (b) linear oligoundecanoates (**10**), and (c) an expansion of part of the spectrum shown in (b). Samples doped with potassium bromide.

approximately equal amounts: see Fig. 4c for an enlargement of part of Fig. 4b. The linear hexamer, for example, gave $[M+K]^+$ peaks at 1226 (1226) and 1224 (1224). Even though the linear oligomers were >97% pure by ^{1}H NMR spectral and

GPC analyses, for most of the linear oligomers there were also peaks suggesting the presence of OH, in place of Br, end groups. The hexamer, for example, showed a mass peak at 1162 (1162). Similarly, the spectrum also showed strong peaks at 592 (592) and 776 (776), and weaker peaks at 960 (960) and 1144 (1144) attributable, respectively, to the cyclic trimer through to the cyclic hexamer. In this connection it is interesting to note that the spectrum of a synthetic 50 : 50 mixture of the cyclic and linear oligomers only showed significant peaks for the cyclic oligomers, indicating that the cyclics are much more easily detected than the linears. These observations serve to emphasise that the intensities of mass peaks in MALDI-ToF mass spectra are certainly not simply proportional to the amount of that molecular species present in the mixture.

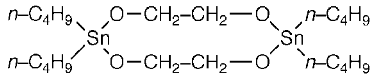
Cyclo-oligomerisation using other catalysts

Many catalysts have been used in the past to achieve the CDP of polyesters. Using GPC analysis to monitor the reactions, it was a simple matter to test their performance in the present system. Of those studied before, dibutyltin oxide (**13**)[21,36] performed essentially as well as dibutoxydibutyltin (**9**) and the use of 2 mol% in chlorobenzene at reflux temperature for 6 h gave a 90% yield of cyclic oligoundecanoates (**2**). The dioxastannane (**14**)[21,41] performed almost as well but required a reaction time of 12 h to obtain a 90% yield. This could be reduced to 4 h by using *o*-dichlorobenzene at *ca.* 180 °C. Of other catalysts investigated, 2 mol% of stannous chloride,[26] zinc chloride,[26] ferric chloride[26] or titanium isopropoxide in chlorobenzene at reflux temperature for 7 days gave the cyclic oligomers in yields of only 10–20%, whilst stannous 2-ethylhexanoate,[37] magnesium chloride,[38] manganous chloride,[26] potassium *tert*-butoxide and germanium oxide only gave yields of *ca.* 5%.



$(n\text{-}C_4H_9)_2Sn{=}O$

13



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Fractionation of cyclic oligoundecanoates (2) and re-equilibration studies

To establish that the original CDP product was the equilibrium mixture of cyclic oligomers and to obtain an indication of the relative reactivity of the different cyclics, the products from a larger scale CDP of polyundecanoate (**1**) were fractionated by preparative GPC. The first fraction had the cyclic pentamer (**2**; $n=5$) as the major species present, whilst the last fraction had the cyclic dimer (**12**) as the major species. These two fractions and the pure cyclic monomer (**11**) were then separately treated with 2 mol% of dioxastannane (**14**) in chlorobenzene at reflux temperature. GPC analyses were taken frequently to monitor progress. The progress of the reactions is shown in Fig. 5 and the initial and final percentages of the various cyclics are summarised in Table 2. It is evident that with the two fractions equilibrium was almost reached in 7 h, though the proportions of the different cyclics did change slightly over a further 17 h period. The two products then had essentially the same composition, which was also that of the initial CDP product. The cyclic monomer (**11**) equilibrated much less rapidly and after 48 h the monomer was still the major species present. Even after 7 days equilibrium was not reached. Thus, the cyclic monomer (**11**) is much less reactive than the cyclic oligomers. The ring opening polymerisation of the cyclic monomer (**11**) has been reported before.[43]

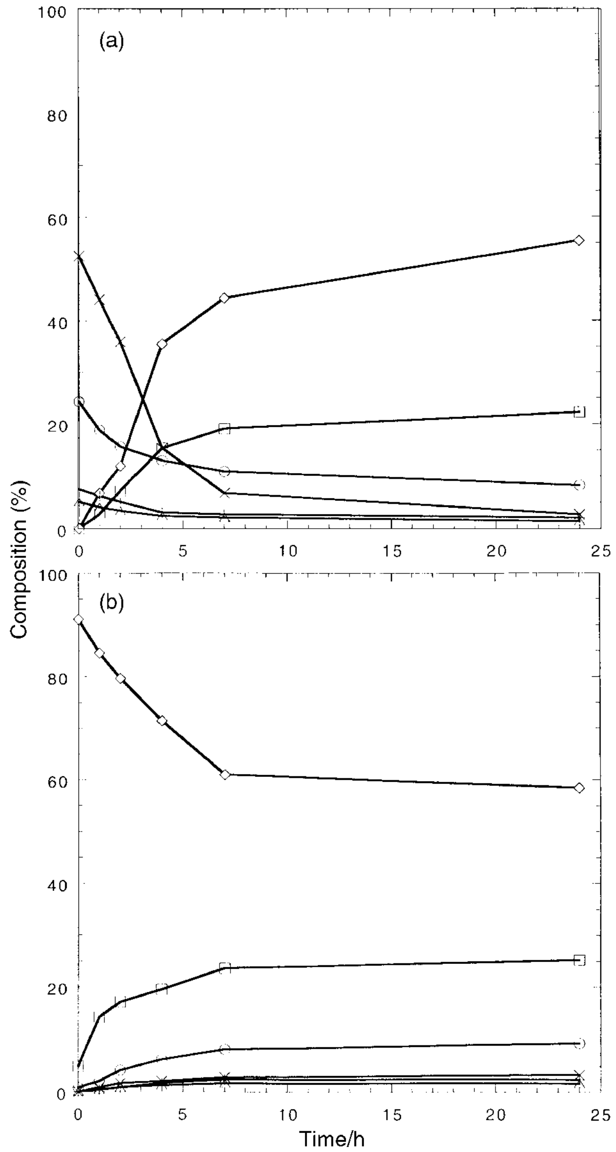

Fig. 5 Progress curves for the equilibration of two fractions consisting of cyclic oligomers (**2**). See text for details of source of fractions and equilibration conditions: (a) starting with fraction consisting mainly of cyclic pentamer and (b) starting with fraction consisting mainly of cyclic dimer. Plot: ◊ = dimer; □ = trimer; ○ = tetramer; × = pentamer; + = hexamer; and △ = heptamer.

Crystal structure of the cyclic undecanoate dimer (12)

Recrystallisation of the final fraction from the preparative GPC experiment discussed above afforded a pure sample of the cyclic dimer (**12**) suitable for an X-ray crystal structure determination, thereby providing further evidence for the cyclic nature of this product. The structure obtained is shown in Fig. 6. It is evident that in the crystal the ring is flattened to give a rectangle with the ester linkages on the shorter edges. The methylene chains along the longer edges have the classical zig-zag arrangement.

Having the pure cyclic dimer in hand allowed the major cyclic species in the GPC trace to be unambiguously assigned.

Synthesis of cyclic octanoates (3), decanoates (4) and dodecanoates (5)

Using the same general procedure described above polyoctanoate (**15**), polydecanoate (**6**) and polydodecanoate (**16**) were prepared from the corresponding[39] ω-bromo acids. The required C_8 and C_{12} compounds were available commercially. 10-Bromodecanoic acid was prepared by oxidising the

Table 2 Comparison of reaction product compositions in re-equilibrations of various cyclic oligomers[a]

	Percentage of cyclic *n*-mers by weight[b]						
	First fraction[c]		Last fraction[c]		Cyclic monomer		
n-Mers	Initially	After 24 h	Initially	After 24 h	Initially	After 24 h	After 7 days
1	0	0.7	1.0	0.9	100	70	40
2	0	59	93	58	0	21	30
3	1.0	23	4.4	25	0	6.2	14
4	26	8.4	0.7	9.0	0	1.9	7.8
5	57	3.3	0.6	3.3	0	0.5	3.9
6	8.4	1.5	0.2	1.6	0	0.2	2.0
7	5.6	0.8	0.1	1.0	0	0.1	1.4
8	0.7	0.4	0	0.5	0	0.1	0.7
>8	1.3	0.9	0	0.7	0	0	0.2

[a]Reactions carried out at 130° using 2 mol% of compound **14** as the catalyst. [b]By GPC analysis. Percentage composition by weight. [c]These fractions were obtained by the preparative GPC of cyclic oligoundecanoates (**2**)

commercially available 11-bromoundec-1-ene with sodium periodate and a catalytic amount of potassium permanganate.[44] The molecular weights of the linear polymers are given in the Experimental section. These linear polymers were cyclo-depolymerised using 2 mol% of dibutoxydibutyltin (**9**) as the catalyst in chlorobenzene at reflux temperature for 8 h to give the corresponding cyclic oligomers (**3**)–(**5**) in good yields. Table 1 summarises the compositions of the cyclic products as determined by GPC analysis. With these starting polymers, as expected, the cyclic dimers were the major products, the cyclic monomers being too strained to be formed in more than minor amounts.[40] Comparison of the yields of the various cyclics from these three polymers with the yields obtained from the CDP of polyundecanoate (**1**) suggests there may be an odd–even effect in the distribution of ring sizes.

Some ring-opening polymerisations of cyclic oligoundecanoates (2)

As noted in the Introduction, cyclic oligomers are of interest as feedstocks for ED-ROP. The novelty with these polymerisations is that they are not driven by the release of ring strain, but entropically. The polymerisation is simply the reverse of the CDP but since the equilibration is carried out at high concentration, in practice the neat cyclic oligomers, and not under dilute solution conditions, the equilibrium favours the polymer. Moreover, since in the present case, for example, the number of ester linkages in the linear product is virtually the same as in the cyclic oligomers, essentially no heat is evolved. Furthermore, because the process is just a reshuffling of ester linkages, no small molecules are evolved in the polymerisation. These various features make the process environmentally-friendly.

Mixtures of the cyclic oligoundecanoates (**2**) with 2 mol% of dioxastannane (**14**) were cast on microscope slides using dichloromethane. The slides were then heated in a vacuum for various periods to bring about polymerisation. The reactions were carried out above the mp (83 °C) of the polymeric product but below its decomposition temperature (*ca.* 195 °C). Table 3 summarises the results. With a temperature of 170 °C, for example, and a reaction time of 48 h the cyclic oligomers were transformed into polyundecanoate (**1**) with an M_n of 46 200 and an M_w of 81 600: see entry 4. These values are significantly higher than those achieved by the initial phase transfer catalysed synthesis described above,[39] and the ring opening polymerisations of the cyclic monomer (**11**) and its C_{12} homolog carried out in bulk with alkali metal methoxide catalysis at 120 °C.[43] As expected for an equilibrium process, the ratio of M_n and M_w is close to 2. Lithium stearate[8] was a much less effective catalyst: see entry 5. Polymerisation of the neat cyclic monomer (**11**) at 170 °C, at or below abnospheric pressure, was not feasible on account of its volatility. It is interesting to note that a CDP reaction of the type carried out by Spanagel and Carothers[38] coupled with the ring-opening polymerisation, provides an attractive basis for re-cycling the polymer.

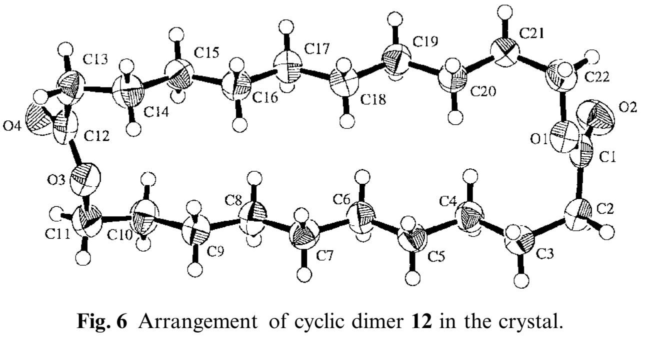

Fig. 6 Arrangement of cyclic dimer **12** in the crystal.

Conclusions

The cyclo-depolymerisation of linear polyundecanoate (**1**) has been studied in some detail. The cyclic oligomers (**2**) obtained were characterised by gel permeation chromatography, ^{1}H NMR spectroscopy and mass spectroscopy in comparison with the corresponding linear oligomers. The cyclic dimer (**12**) was isolated and its crystal structure determined. Cyclic oligo-octanoates (**3**), oligodecanoates (**4**) and oligododecanoates (**5**) were prepared similarly. As a result of these studies it will be easy in future to monitor novel potential syntheses of these cyclic oligomers. The ring-opening polymerisation of the cyclic oligoundecanoates (**2**) was briefly investigated. This environmentally-friendly process afforded polymer (**1**) with higher molecular weights than the initial phase transfer catalysed polymerisation.[39] Other ED-ROP are currently being investigated.

Experimental

All reagents were used as purchased except for magnesium chloride, tin(II) chloride, manganese(II) chloride and iron(ii) chloride which were dried at 60 °C *in vacuo* overnight prior to use. Dibutoxydibutyltin (**9**) and dibutyltin oxide (**13**) were purchased from Aldrich Chemical Company. Dioxastannoxane (**14**) was prepared by the literature method.[21,42]

Organic solutions were dried using magnesium sulfate. Unless indicated otherwise, melting points (mp) were measured using a Gallenkamp Melting Point Apparatus and are uncorrected. Infra-red (IR) spectra were recorded on a Perkin-Elmer 1710 Fourier transform (FT) instrument for, unless indicated otherwise, KBr discs. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 500 Mz using a Varian Unity Spectrometer for solutions in deuteriochloro-

Table 3 Ring-opening polymerisations carried out using the neat cyclic oligomers[a]

		Reaction conditions		Molecular weights of product[c]		
Entry	Catalyst[b]	T/°C	t/h	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	Compound (**14**)	130	20	17 400	36 700	2.11
2	Compound (**14**)	130	92	34 300	78 400	2.29
3	Compound (**14**)	170	20	15 200	25 700	1.69
4	Compound (**14**)	170	48	46 200	81 600	1.77
5	Lithium stearate	170	24	5200	10 400	2.00

[a]As a film on a microscope slide cast from a dichloromethane solution of cyclic oligoundecanoates (**2**), obtained by the CDP of polymer (**1**). [b]2 mol% of catalyst added. [c]By GPC relative to polystyrene standards.

form. MALDI-ToF mass spectrometry was carried out on a Kratos Kompact MALDI 3 using a dithranol matrix doped with potassium bromide. For polymer synthesis and for ring opening studies GPC analysis was carried out using a system incorporating a Knauer 64 pump operating at a flow rate of 1 cm^3 min^{-1} through two Polymer Lab 10 μ Mixed B and I 500 Å columns followed by a Waters 410 differential refractometer for detection with tetrahydrofuran as the eluant. The columns were calibrated using polystyrene standards. For depolymerisation studies a GPC system was used which incorporated a Gilson 307 pump operating at a flow rate of 0.3 cm^3 min^{-1} through four Polymer Labs 3 μ Mixed E columns in tandem followed by a GBC LC 1240 Differential Refractometer for detection. The eluant was chloroform. Preparative GPC was carried out using a Waters 590 HPLC pump operating at a flow rate of 10 cm^3 min^{-1} through a 500 Å preparative Styragel column followed by a Waters R403 Differential Refractometer. Toluene was the eluant. DSC and TGA were carried out on a Seiko SSC/5200 machine.

Polyundecanoate (1)[39]

11-Bromoundecanoic acid (50 g) was dissolved in chlorobenzene (50 ml). Tetra-*n*-butylammonium hydroxide (112 ml of a 40% w/v aqueous solution) was added to achieve neutralisation with phenolphthalein (1% in isopropanol) as the indicator. The two-phase reaction was heated under reflux with vigorous stirring for 36 h. The mixture was then cooled and poured into acidified methanol (50 ml concentrated sulfuric acid in 500 ml methanol) at 0 °C. The sticky solid which precipitated was rapidly (to minimise the possibility of transesterification) filtered off, redissolved in the minimum amount of chloroform and reprecipitated into methanol (1 litre). The white flakes which formed were collected by filtration and dried at 40 °C under vacuum (0.2 mm of Hg) (32.5 g, 94% yield); mp 83 °C, (by DSC). By GPC (THF) it had M_n 23 200 and M_w 41 600. TGA showed decomposition above 193 °C.

Cyclo-depolymerisation of polyundecanoate (1)

The polyundecanoate (**1**) (500 mg, 2.71 mmol) and the dibutoxydibutyltin (**9**) (0.05 mmol) were dissolved in chlorobenzene (25 ml). The reaction mixture was heated under reflux for 8 h. The mixture was then cooled and the solvent rapidly evaporated off at 1.0 mm of Hg (to minimise the possibility of the equilibrium being shifted) to leave the crude product (450 mg; 90%). It had ν_{max} 1729 cm^{-1} and δ 4.07 (t, $J=6.5$ Hz; 4H; CH_2OCO), 2.34 (t, $J=6.5$ Hz; 4H; CH_2CH_2COO), 1.65 (quintet, $J=6.5$ Hz; 8H; CH_2) and 1.34 ppm (s, 18H, CH_2). The GPC trace for the product is shown in Fig. 1. The MALDI-ToF mass spectrum is shown in Fig. 4a.

Preparative GPC fractionation of the products from cyclo-depolymerisation of polyundecanoate (1)

Polyundecanoate (**1**) (3.50 g; 19 mmol) and dibutoxydibutyltin (**9**) (100 mg, 0.34 mmol) were dissolved in chlorobenzene (200 ml). The reaction was heated under reflux for 8 h. The solvent was then removed by distillation under reduced pressure (1.0 mm of Hg). The crude solid was fractionated on a preparative GPC column using toluene as solvent. The solid was added to the column as a solution in toluene–chloroform [5 : 1] (20 ml). The flow rate was 10 ml min^{-1}. After 2 h the collection of fractions (50 ml) was commenced and a total of 35 fractions were collected. Fractions 1–12 were discarded as the amounts were <10 mg and fractions 33–35 because they contained only solvent impurities. The remaining fractions were combined to give four major fractions. The first of these (506 mg), eluted early, and last (1129 mg) had the compositions given in Table 2. These fractions were used for the further experiments described below.

Re-equilibration of cyclic fractions using dioxastannane (14)

(a) The first cyclic fraction from the preceding experiment (250 mg) and dioxastannane (**14**) (11 mg) were dissolved in chlorobenzene (15 ml). The reaction was heated under reflux. Samples (0.5 ml) were taken after 1, 2, 4, 7 and 24 h and analysed by GPC (chloroform). The results are summarised in Fig. 5a and Table 2.

(b) The final cyclic fraction from the preceding experiment was equilibrated and the reaction monitored as in (a). The results are summarised in Fig. 5b and Table 2.

Reaction of undecanolactone (11) with dioxastannoxane (14)

The lactone (**11**) (507 mg, 2.75 mmol) and dioxastannoxane (**14**) (14 mg, 0.024 mmol) were dissolved in chlorobenzene (30 ml). The mixture was heated under reflux. Samples (0.5 ml) were taken at 1, 2, 5, and 7 days and analysed by GPC (chloroform). The key results are summarised in Table 2.

10-Bromodecanoic acid[44]

To an ice-cold suspension of 11-bromoundec-1-ene (27.0 g) was added potassium carbonate (41.5 g), sodium periodate (110.0 g) and potassium permanganate (7.3 g). After the initial reaction subsided the mixture was stirred for 20 h and allowed to come to room temperature. Sodium metabisulfite was added carefully until the mixture became pale yellow. The solution was then washed with ethyl acetate (3 × 50 ml). The aqueous solution was acidified with hydrochloric acid (2 M) and extracted into chloroform (3 × 50 ml). The combined extracts were dried and the solvent evaporated off. This afforded the crude product (20.0 g). Recrystallisation from water gave white needles (12.2 g; 42%), mp 40–41 °C (lit.,[45] 42 °C).

Polyoctanoate (15), polydecanoate (6) and polydodecanoate (16)

These were prepared from the appropriate ω-bromo acids using the procedure described above for the preparation of polyundecanoate (**1**). GPC analyses were carried out using the system with THF as the eluant. The polyoctanoate (**15**) had M_n 9700 and M_w 17 300; the polydecanoate (**6**) had M_n 12 400, and M_w 22 500; and the polydodecanoate (**16**) had M_n 14 700 and M_w 24 800.

Cyclo-depolymerisations of polyoctanoate (15), polydecanoate (6) and polydodecanoate (16)

These polymers were cyclo-depolymerised using just the same procedure as that used with polyundecanoate (**1**). The GPC analyses of the cyclic products are summarised in Table 1.

Ring-opening of cyclic oligoundecanoates (2) catalysed by dioxastannoxane (14)

The following experiment (that summarised in Entry 4) is typical of those summarised in Table 3.

The cyclic oligoundecanoates (**2**) (25 mg), from the CDP of polymer (**1**), were dissolved in dichloromethane (2 ml) containing the tin catalyst (**14**) (16.2 mg in 100 ml dichloromethane). The solution was applied to a microscope slide and the solvent allowed to evaporate. The slide was then placed in a small vaccum oven (0.1 mmHg) and heated at 170 °C. At 24 hour periods the plate was removed and allowed to cool to room temperature. A sample was removed and analysed by GPC (THF). The results are summarised in Table 3.

Crystal structure determination of the cyclic dimer (12)†

The last major fraction from the preparative GPC fractionation reported above was recrystallised three times from ethanol. This gave crystals, mp 65–66 °C (lit.,[46] 73–74 °C), suitable for a crystal structure determination. GPC analysis (chloroform) gave a single peak with a retention volume of 33.7 cm^3, thus allowing the remaining cyclic oligomer peaks to be assigned. Attempts to obtain a MALDI-ToF mass spectrum were unsatisfactory due to the presence of peaks resulting from the matrix, but using chemical ionization mass spectrometry it had m/z 386 (100%, $[M+NH_4]^+$).

Crystal data. $C_{22}H_{40}O_4$, $M=368.56$, monoclinic, $a=27.653(7)$, $b=8.130(2)$, $c=9.857(4)$ Å, $\beta=95.74(4)°$, $U=2205(2)$ Å^3, $T=290$ K, space group $P2_1/c$ (no. 14), $Z=4$, $\mu_{\mathrm{MoK}\alpha}=0.069$ mm^{-1}, 4486 reflections measured, 4226 unique ($R_{\mathrm{int}}=0.030$), 1767 with $I>3\sigma(I)$ which were used in the refinement of 235 parameters. The final R and R_w were 0.050 and 0.035, respectively. Fig. 6 illustrates the structure.

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