Synthesis of a series of cyclic oligo(alkylidene isophthalate)s by cyclo-depolymerisation

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Abstract

The synthesis of series of cyclic oligo(alkylidene isophthalate)s by the cyclo-depolymerisation of the corresponding linear polymers has been investigated and the yields of the various cyclic oligomers determined as a function of the polymer structure. With up to 15 ring atoms per repeat unit the main products are the cyclic dimers (up to 90% yield) with smaller amounts of the larger rings. When there are more than 16 ring atoms per repeat unit the main products are the cyclic monomers (up to 72% yield) with smaller amounts of the larger rings. Possible applications for such cyclic oligomers are discussed including their possible use as feedstocks for environmentally friendly entropically driven ring-opening polymerisations and as building blocks for novel polymeric structures. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclic oligoesters; Cyclo-depolymerisation

1. Introduction

Cyclic oligomers have been known for many years as minor components in the products of step-growth polymerisations [1–3]. Recently, however, there has been an increased interest in the cyclic oligomers themselves [4–6], mainly because of their potential for use as feedstocks for environmentally friendly entropically driven ring-opening polymerisations (ED-ROP) [4,7–9], but also, to a lesser extent, as recognition systems [10–12] and as building blocks for novel materials [6,13]. As a consequence, the synthesis of cyclic oligomers is currently a very active research area and cyclic oligomers have recently been synthesised by high-dilution methods [9,14–19], polymer-supported methods [20–24], and cyclo-depolymerisations [25–34]. The classes of cyclic oligomers prepared include carboxylate esters [9,23,25–32], carbonates [8], amides [19–22,24], and high performance aromatic ether ketones [15,17,18,33] and sulphones [14,16,18,33,34].

In order to prepare certain types of novel polymeric materials it is desirable to have available a range of functionalised cyclic oligomers which can serve as building blocks and be chemically linked to other molecules as appropriate. As 5-substituted isophthalic acids (**1**) and (**2**) are commercially available, and several others can be prepared

easily from these, they are attractive starting materials for the synthesis of functionalised cyclic oligomers, especially as the symmetry of the 5-substituted acids means that, within a given series of cyclic oligomers, there is only one possible cyclic dimer, one cyclic trimer, etc. As a prelude to the synthesis of functionalised cyclic oligomers, we have studied the synthesis of a series of cyclic oligo(alkylidene isophthalate)s by the cyclo-depolymerisation of the corresponding linear polymers (see Scheme 1) and we report the results here. The main aims were to determine which sizes of rings could be prepared easily and in useful yields. A few of the present cyclic oligo(alkylidene isophthalate)s have been prepared before. Two were prepared by the cyclo-depolymerisation of linear polymers [32], and four were prepared from isophthaloyl dichloride and diols using a novel pseudo-high dilution procedure [9]. However, no broad systematic studies have been carried out. Previous work will be referred to appropriately.
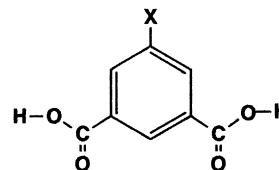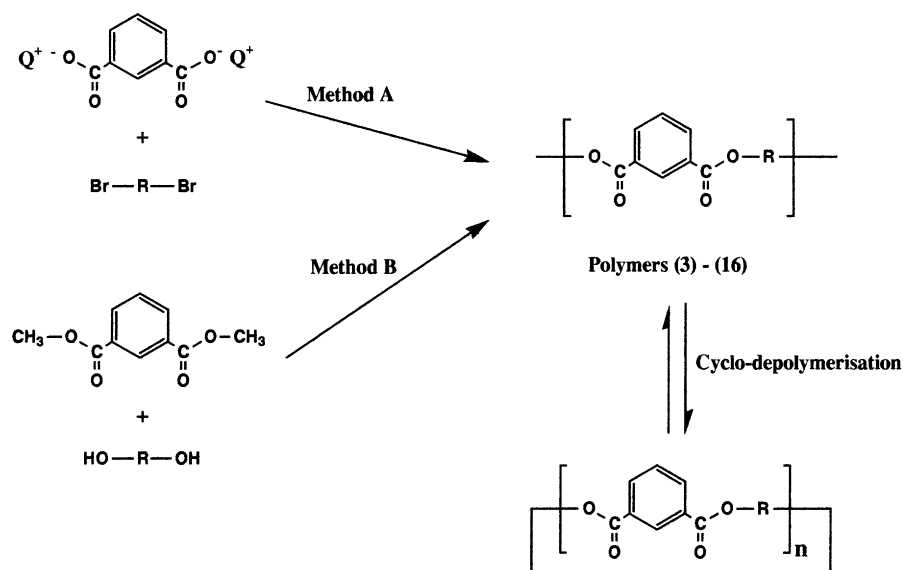

(1) : -OH

(2) : -NO₂

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Scheme 1. Synthesis of linear poly(alkylidene isophthalate)s (**3**)–(**16**) by Methods A and B and the cyclo-depolymerisation of these polymers. Q^+ quaternary quaternary ammonium cation, i.e. tetra-*n*-butylammonium.

2. Experimental

2.1. General experimental details

All the reagents and solvents were used as received. Melting points (mp) were obtained on a Gallenkamp apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin–Elmer 1710 Fourier Transform (FT) instrument for, unless otherwise indicated, evaporated films (from dichloromethane). ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz on an Inova 300 instrument for, unless otherwise indicated, solutions in deuteriochloroform. Electron Impact (EI) and Chemical

Ionisation (CI) mass spectra were obtained on a VG Trio 2000 instrument. Matrix Assisted Laser Desorption Ionisation–Time Of Flight (MALDI–TOF) mass spectra were obtained using a Micromass Tof Spec 2e instrument. Gel permeation chromatography (GPC) of cyclic oligomers was performed using a PLGel Mixed-E, 4 column set with chloroform as the eluent. Unless indicated otherwise GPC of linear polymers was performed using a PLGel 30 cm, 10 μ Mixed B (×2) and 500 Å (×1) 3-column set with tetrahydrofuran as the eluent. Each column set was calibrated using a series of polystyrene standards, each with a narrow polydispersity. The data was collected and analysed using software created and developed by the Manchester

Table 1

Synthesis of poly(alkylidene isophthalate)s by phase transfer catalysed reactions (see Section 2 for details of a typical synthesis)

Polymer	Starting dibromide	Procedure[a]	Reaction time (h)	Yield (%)	M_n[b]	M_w[b]	DP[c]
(**3a**)	Br–$(CH_2)_2$–Br	I	72	77	1600	2100	17
(**4**)	Br–$(CH_2)_3$–Br	II	168	83	5300	10 800	51
(**5a**)	Br–$(CH_2)_4$–Br	I	71	98	13 800[d]	37 700[d]	125
(**6**)	Br–$(CH_2)_5$–Br	II	168	71	4700	12 400	40
(7)	Br–$(CH_2)_6$–Br	I	78	72	15 500	34 000	125
(**8**)	Br–$(CH_2)_7$–Br	II	168	37	2200	3900	17
(**9**)	Br–$(CH_2)_8$–Br	I	162	85	8500	20 700	62
(**10**)	Br–$(CH_2)_9$–Br	I	168	66	6100	18 200	42
(**11**)	Br–$(CH_2)_{10}$–Br	II	168	51	9400	22 100	62
(**12**)	Br–$(CH_2)_{11}$–Br	I	168	96	14 100	59 200	89

[a] Procedure I—chloroform as organic phase; Procedure II—1,2-dichlorobenzene as organic phase (Section 2).

[b] Unless indicated otherwise, GPC was performed using THF as the eluent. Values quoted are relative to polystyrene standards.

[c] Based on M_n value. DP = Average number of ester linkages formed plus one.

[d] GPC performed using chloroform as eluent (RAPRA).

Table 2
Synthesis of poly(alkylidene isophthalate)s by transesterification (see Section 2 for details of a typical synthesis)

Polymer	Starting diol	Procedure[a]	Yield (%)	M_n[b]	M_w[b]	DP[c]
(3b)	HO–$(CH_2)_2$–OH	I	90	10 000	27 000	104
(5b)	HO–$(CH_2)_4$–OH	I	81	6600[d]	23 900[d]	60
(13)	HO–$(CH_2)_{12}$–OH	II	42	24 900	44 500	150
(14)	HO–$(CH_2CH_2O)_2$–H	I	88	6000	13 100	51
(15)	HO–$(CH_2CH_2O)_3$–H	I	85	8700	21 700	62
(16)	HO–$(CH_2CH_2O)_4$–H	II	64	11 800	19 600	73

[a] Procedure I—two-step process; Procedure II—one-step process (Section 2).
[b] Unless indicated otherwise, GPC was performed using THF as the eluent. Values quoted are relative to polystyrene standards.
[c] Based on M_n value. DP = Average number of ester linkages formed plus one.
[d] GPC performed using chloroform as eluent (RAPRA).

Polymer Group from Lab VIEW software (National Instruments). We thank RAPRA (Shawbury) for some GPC measurements (see Tables 1 and 2).

2.2. Polymer synthesis using liquid–liquid phase transfer catalysis (Method A) [35]

Two procedures were used, which differed only in the choice of organic solvent and reaction temperature. Procedure I refers to the use of chloroform as the organic phase (reaction temperature ca. 60°C); Procedure II uses 1,2-dichlorobenzene (reaction temperature ca. 100°C). A typical synthesis is given below. Polymers (3a), (4), (5a), (6) and (8)–(12) were prepared similarly using the conditions and procedures, and with the results, summarised in Table 1.

2.2.1. Synthesis of poly(hexylene isophthalate) (7) using Procedure I

Isophthalic acid (8,31 g, 0.05 mol) and distilled water (30 cm³) were mixed and a drop of phenolphthalein indicator solution (1% (w/w) in water) was added. A 40% aqueous tetra-*n*-butylammonium hydroxide solution (71.35 g, 0.11 mol) was added until the mixture was just alkaline. This gave the soluble dicarboxylate salt. To the resulting solution was added 1,6-dibromohexane (12.20 g, 0.05 mol), dissolved in chloroform (50 cm³). The two-phase system was stirred vigorously and heated under reflux for 78 h. After this time, the reaction mixture was allowed to cool and was then added with stirring to methanol (1.25 l). This precipitated the polymeric product. The product was filtered off, washed with methanol and dried in vacuo (20 mm of Hg; 50°C) to give the crude polymer. The polymer was purified by precipitation from chloroform into methanol to give poly(hexylene isophthalate) (7) (8.94 g, 72% yield). It had ν_{max} 2933, 2896, 2855, 1721, 1302, 1237, and 729 cm^{-1}; and δ (CDCl₃ solution) 1.56 (broad m, 4H), 1.85 (broad m, 4H), 4.39 (broad t, 4H), 7.55 (broad t, 1H), 8.24 (broad dd, 2H), and 8.70 (broad m, 1H) ppm. GPC data (THF) are summarised in Table 1.

2.3. Polymer synthesis using transesterification (Method B)

Two procedures were used. Procedure I was employed when lower boiling glycols were used, while Procedure II was followed when using the higher boiling glycols. Typical syntheses are given later. Polymers (5b) and (13)–(15) were prepared similarly as indicated in Table 2.

2.3.1. Synthesis of poly(ethylene isophthalate) (3b) using Procedure I

Step 1: Preparation of "bis-(hydroxyethyl) isophthalate". Dimethyl isophthalate (194.2 g, 1.0 mol) and ethylene glycol (136.4 g, 2.2 mol) (shown to be free of diethylene-glycol by ^{1}H NMR spectroscopy) were heated to 140°C under a stream of nitrogen. Manganese acetate tetrahydrate (0.1 g, 0.41 mmol) was then added and the temperature of the reaction was raised over 20 min to 190°C and then over 2.5 h to 230°C. As the temperature increased, methanol formed by transesterification was removed by distillation through a Vigreux column, thus driving the reaction. When collection of methanol ceased (68 cm³, 53.8 g, 1.74 mol), the crude white solid, containing excess ethylene glycol, was recovered (210 g, 83% yield) and used in Step 2. Analysis by GPC at this stage indicated the presence of a series of linear oligomers (DP = 1–10).

Step 2: Polymerisation. The oligomeric product from the above reaction (210 g) was heated in the presence of titanium isopropoxide (0.57 g, 2 mmol), with mechanical stirring, to 160°C to effect melting. The system was then carefully evacuated using an oil pump then flushed with argon. This process was repeated twice before the final vacuum was applied (<1 mm of Hg). The temperature of the reaction mixture was raised in 10° increments to 300°C (over 3.5 h), during which time polymerisation occurred. This led to an increase in the viscosity of the reaction mixture. The crude polymeric product was removed from the vessel while still hot, and hence molten, and left to cool. This crude product was purified as required by precipitation from chloroform into methanol. Typically the crude polymer (10 g) in chloroform (40 cm³) was added dropwise to ~1 l methanol. The polymer, collected by filtration, was

Table 3
Cyclo-depolymerisation of poly(alkylidene isophthalate)s

Starting polymer	Procedure[a]	Yield (%)	Ring atoms per repeat unit	Composition of product: Percentage yields of cyclic n-mers by weight									MALDI–ToF MS[b]
				$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=>8$[c]	
(3b)	I	54[d]	9	0	54	6.0	7.0	6.0	6.0	8.0	–	7	8
(3b)	III	100	9	0	90[e]	2.4	1.2	0.6	–	–	–	6[f]	–
(4)	II	72	10	0	29	26	14	8.5	5.1	3.4	2.5	12	–
(5b)	III	95	11	0	48	19	12	7.8	4.9	3.3	2.0	4	14
(6)	II	68	12	0	47	26	14	6.6	3.6	1.3	0.7	1	–
(7)	II	91	13	0	51	19	11	6.9	4.5	3.2	1.8	3	–
(7)	III	97	13	0	48	19	11	7.3	4.9	3.3	2.4	6	17
(8)	II	96	14	0	39	23	12	6.9	4.1	2.5	1.6	12	–
(9)	III	99	15	14	27	15	9.2	5.9	4.2	3.2	2.7	19	10
(10)	II	93	16	56	18	8.6	4.0	3.3	–	–	–	10	–
(11)	III	99	17	68	13	5.0	2.8	2.0	1.3	–	–	8	6
(12)	II	88	18	63[e]	21	7.3	3.3	–	–	–	–	6	–
(13)	I	99	19	72	13	3.0	–	–	–	–	–	12	–
(14)	III	99	12	0	41	21	11	6.6	4.1	2.7	–	14	11
(15)	III	99	15	14	36	17	8.2	5.5	3.1	–	–	17	10
(16)	I	96	18	58[e]	13	8.0	5.0	2.0	1.0	–	–	13	–

[a] See Section 2 for details. Procedure I—chlorobenzene as solvent, polymer concentration = 1.25% (w/v), 4 day reaction period; Procedure II—1,2-dichlorobenzene as solvent, polymer concentration = 1.00% (w/v), 10 days; and Procedure III—1,2-dichlorobenzene as solvent, polymer concentration = 2.00% (w/v), 10 days.

[b] Selected samples were studied by MALDI–TOF mass spectrometry. Peaks due to cyclics were seen clearly from $n=2$ up to the values given.

[c] Values include mainly unidentified higher cyclic oligomers, and, in some cases, minor amount of small linear oligomers.

[d] A substantial amount of solid remaining at the end of the reaction period was filtered off. It was identified as the cyclic dimer (17).

[e] A pure sample of this cyclic compound was isolated.

[f] 2.7% due to E_1E_2 dimer; 0.9% due to $E_1E_1E_2$ trimer.

obtained as a white solid (typically in 90% yield). It had ν_{max} 2957, 1723, 1297, 1225, 1135, 1095, 1076, and 727 cm^{-1}; and δ (CDCl$_3$ solution) 4.68 (broad s, 4H), 7.49–7.54 (broad t, 1H), 8.20–8.23 (broad dd, 2H), and 8.70 (broad s, 1H) ppm. Small peaks approximately 0.1 δ upfield from those quoted earlier are also seen in the ^{1}H NMR spectrum. These are attributed to the presence of ca. 3% of the cyclic dimer. GPC data (THF) are summarised in Table 2.

2.3.2. Procedure II is illustrated by the preparation of poly(tetraethylene glycol isophthalate) (16)

Dimethyl isophthalate (168.0 g, 0.87 mol) and tetraethylene glycol (150 cm^3, 0.87 mol) were heated, with stirring, to 110°C in the presence of titanium tetra-iso-propoxide (0.49 g, 1.7 mmol). The mixture was a homogeneous liquid. The system was evacuated using an oil pump and then flushed with argon. This process was repeated twice before applying the final vacuum (2 mm of Hg). The reaction temperature was progressively raised to 300°C over a period of 4.5 h, until the viscosity of the mixture appeared to have increased. The dark brown polymer (266.5 g, 95%) was removed from the vessel while still hot and allowed to cool. GPC analysis showed the crude polymer to have $\overline{M}_n =$ 7971 and $\overline{M}_w = 16202$. The crude polymer was purified by precipitation from ethyl acetate into methanol. The final polymer (16) (64% yield) had ν_{max} 2873, 1723, 1304, 1239, 1127, 1097, 1078 and 730 cm^{-1}; and δ (CDCl$_3$ solution) 3.65 (broad s, 8H), 3.8 (broad t, 4H), 4.5 (broad t, 4H), 7.5 (broad t, 1H), 8.2 (broad dd, 2H), and 8.7 (broad s, 1H) ppm. GPC data (THF) are summarised in Table 2.

2.4. Cyclo-depolymerisation procedures

Various methods were used. The differences between the methods are the solvents employed (and hence the reaction temperatures) and the initial concentrations of linear polymer. Procedure I—refers to the use of chlorobenzene as the reaction solvent and an initial polymer concentration of 1.25% (w/v); Procedure II—1,2-dichlorobenzene as the reaction solvent and a polymer concentration of 1.00% (w/v); Procedure III—1,2-dichlorobenzene as the reaction solvent and a polymer concentration of 2.00% (w/v). The following method is typical. See Table 3 for the procedures used with each polymer and a summary of the results obtained.

2.4.1. CDP of poly(hexylene isophthalate) (7) using Procedure III

Poly(hexylene isophthalate) (7) (2.5 g, 10 mmol.) was heated at reflux temperature in dry 1,2-dichlorobenzene (125 cm^3) in the presence of dibutyltin oxide (75 mg, 0.30 mmol; 3 mol% based on the polymer repeat unit). The reaction was allowed to proceed for 10 days, with samples being taken periodically for analysis by GPC (chloroform) until the proportions of cyclic oligomers did not change any more. After 10 days the reaction was

removed from the heat. No precipitation was observed on cooling the mixture to room temperature. The solution was then reduced to dryness under vacuum (20 mm of Hg) to give an off-white solid (2.43 g, 97% yield). It had ν_{max} 2936, 2861, 1723, 1309, 1237, 1142, 1096, 1074 and 727 cm^{-1}; and δ (CDCl$_3$ solution) 1.54–1.65 (broad m, 4H), 1.84 (broad m, 4H), 4.34–4.41(broad m, 4H), 7.57 (broad m,1H), 8.25 (broad m, 2H), and 8.70–8.74 ppm (broad m, 1H). GPC data (CHCl$_3$) are summarised in Table 3.

2.5. Isolation of cyclic dimer (17) from the cyclo-depolymerisation of polymer (3b)

The cyclo-depolymerisation of polymer (3b) using Procedure III (i.e. second entry in Table 3) afforded a precipitate which increased in amount as the reaction progressed. This proved to be the cyclic dimer (17) (82% yield). It was monodisperse by GPC (CHCl$_3$) and had m.p. 333–335°C (Ref. [36], 325–327°C); ν_{max} 2917, 1719, 1453, 1371, 1296, 1247, 1130, 1074 and 729 cm^{-1}; and δ 4.73 (s, 4H), 7.65 (t, 1H), 8.35 (dd, 2H) and 8.94 (s, 1H); m/z (CI) 402[100%, $(M + NH_4)^+$].

2.6. Isolation of cyclic monomer (18) from the cyclo-depolymerisation of polymer (12)

A portion of the cyclic mixture (1.0 g) from the cyclo-depolymerisation of polymer (12) was fractionated by preparative GPC (toluene). The first fraction to elute was identified as compound (18), (0.44 g, 44%), m.p. 88–89°C. It had ν_{max} 1715 cm^{-1}; δ (CDCl$_3$, 200 MHz) 1.4 (16H, m, CH$_2$), 1.8 (4H, m, C$\underline{H}_2$CH$_2$O), 4.4 (4H, t, $J = 5.5$ Hz, CH$_2$O), 7.55 (1H, t, $J = 7.5$ Hz, H-5), 8.3 (2H, d, $J = 7.5$ Hz, H-4), and 8.55 ppm (1H, s, H-2); m/z (CI) 350[100%, $(M + NH_4)^+$].

2.7. Isolation of cyclic monomer (19) from the cyclo-depolymerisation of polymer (16)

A portion of the cyclic mixture (2.5 g) from the cyclo-depolymerisation of polymer (16) was fractionated by silica gel column chromatography with ethyl acetate as the eluent. Column fractions were analysed by TLC and appropriate fractions combined. The first eluted material was identified as compound (19) (0.72 g, 29%, Rf 0.38), m.p. 87–88°C (Ref. [37], 93–94°C); ν_{max} 1711 cm^{-1}; δ (CDCl$_3$, 200 MHz): 3.75 (8H, s, OC$\underline{H}_2$C$\underline{H}_2$O), 3.8 (4H, t, $J = 4.3$ Hz, CO$_2$CH$_2$CH$_2$O), 4.5 (4H, t, $J = 4.3$ Hz, CO$_2$C$\underline{H}_2$CH$_2$O), 7.55 (1H, t, $J = 7.6$ Hz, H-5), 8.25 (2H, dd, $J = 7.6$ and 1.4 Hz, H-4) and 8.8 ppm (1H, t, $J = 1.4$ Hz, H-2); m/z (CI) 342[100%, $(M + NH_4)^+$].

3. Results and discussion

The synthetic approach adopted for the preparation of the cyclic oligomers was to first prepare linear poly(alkylidene

(18)

(19)

(17)
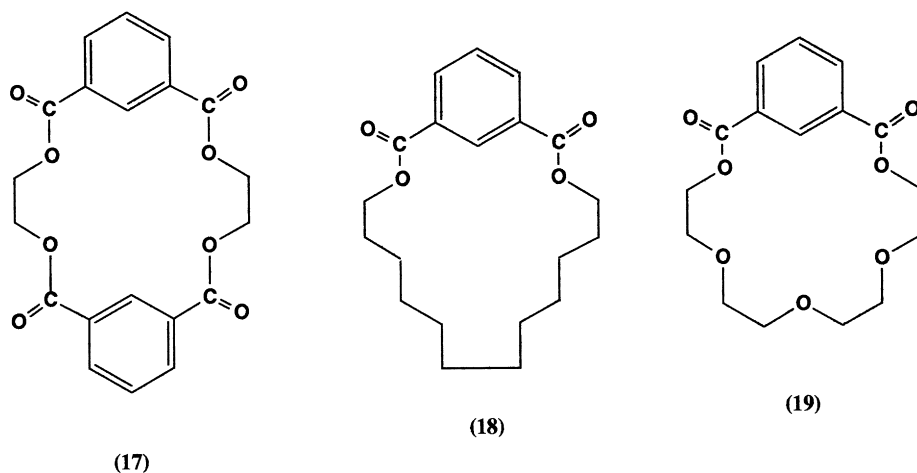
isophthalate)s and then to cyclo-depolymerise these polymers (see Scheme 1).

3.1. Synthesis of linear poly(alkylidene isophthate)s (3)–(16)

Two methods were used to synthesise the poly(alkylidene isophthalate)s. In all cases the polymeric products were characterised by FT-IR and ^{1}H NMR spectroscopy and by GPC.

Method A involved reacting the bis(tetra-*n*-butylammonium) salt of isophthalic acid with the appropriate α,ω-dibromoalkane under phase transfer conditions (see Scheme 1). This method has the attractive feature that the polymerisation conditions are sufficiently mild that they are likely to be tolerant of various functional groups that may be present in functionalised isophthalic acid derivatives. The results obtained are summarised in Table 1. It is evident that, as in previous studies [35], the average degrees of polymerisation ($\overline{DP}$) obtained, i.e. the number of ester linkages formed plus one, are usually >40. Whilst such values are modest if polymers of optimal mechanical performance are required, they are nevertheless adequate for the cyclo-depolymerisation experiments described later. The lowest $\overline{DP}$s were obtained with polymers (3b) and (8). In the former case this is almost certainly for electronic reasons as in our experience the use of ethylene dibromide in similar reactions generally results in modest $\overline{DP}$s. In the case of polymer (8), it is probably due to impurities in the 1,7-dibromoheptane as the $\overline{DP}$ obtained is clearly much less than those achieved with closely similar dibromides.

The second polymerisation method used, Method B in Scheme 1, is the classical transesterification procedure starting with, in the present work, dimethyl isophthalate and the appropriate α,ω-diol. These polymerisations were carried out either as a two-stage process (Procedure I) in which a preliminary transesterification in the presence of manganese acetate was followed by one carried out at 300°C in the presence of titanium isopropoxide, or (Procedure II) as a one-stage process using the latter polymerisation conditions

throughout. The polymerisation procedures used and the results obtained are summarised in Table 2. Clearly the vigorous polymerisation conditions used in these procedures are less likely to be tolerant of functional groups than the conditions used in Method A. It will be noted that polymer (3), which was obtained with a low $\overline{DP}$ by Method A, was now obtained with a $\overline{DP}$ of 104.

3.2. Cyclo-depolymerisation of linear poly(alkylidene isophthalate)s (3)–(16) and characterisation of the cyclic products

The cyclo-depolymerisations (CDPs) were carried out by heating dilute solutions ($\leq$2% (w/v)) of the linear poly(alkylidene isophthalate)s with 3 mol% of dibutyltin oxide [26] in chlorobenzene (b.p. 133°C) or 1,2-dichlorobenzene (b.p. 180°C) at reflux temperature. The reactions were monitored by GPC. Although by GPC analyses excellent yields of cyclics were generally achieved within 12 h, the reactions were carried out for much longer periods in order to obtain an equilibrated, and therefore reproducible, mixture of cyclic oligomers and not a mixture determined by the reaction kinetics. When the proportions of the oligomeric products no longer changed significantly from one analysis to another, the reaction mixture was cooled down and the solvent evaporated off under vacuum. The residue was analysed by FT-IR and ^{1}H NMR spectroscopy, GPC and, in many cases, MALDI–TOF mass spectrometry. The results are summarised in Table 3.

In every case GPC analysis showed that >98% of the product was oligomeric (see Fig. 1 for a typical trace). It also showed that, except for the products from polymer (3b) which will be discussed later, all the resolved peaks were due to just one family of oligomers. Thus, plots of "log $\overline{DP}$" vs. "retention volume" were essentially linear (see Fig. 2 for a typical plot). On theoretical grounds the oligomers were expected to be cyclic [38] and this was indeed the case. This was also expected to be the case from a very simple argument. Thus, if the depolymerisation reduced the $\overline{DP}$ from, for example, 60 to 2.5 then if the oligomers were to be linear
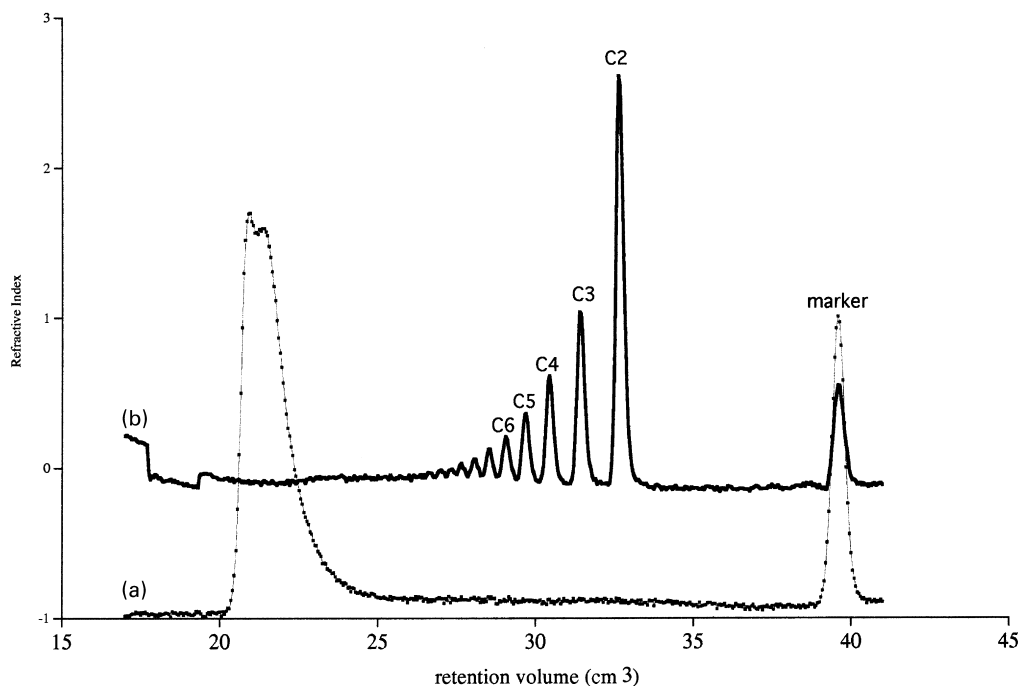
Fig. 1. GPC traces obtained using the "oligomer" column of: (a) poly(hexylidene isophthalate) (**7**). The unusual peak profile arises because a substantial fraction of the sample has a molecular weight above the size exclusion limit of the column; (b) the cyclic oligo(hexylidene isophthalate)s formed by the CDP of polymer (**7**).

there would need to be a 24 fold increase in the number of end groups, and there were simply not enough potential end groups, e.g. water and catalyst fragments, available in the system for this to be possible. Consistent with the oligomers being cyclic no significant signals due to end groups were found in the ^{1}H NMR spectra. Also, as expected [39], once the rings were large enough to be strain free, the amount of each succeeding member of the family decreased as the $\overline{DP}$ increased. In a few cases MALDI–TOF mass spectra were measured (see Table 3). Each of these displayed a clear series of mass peaks at the positions expected for the cyclic oligomers. The ring sizes detected using this technique were in most cases significantly greater than those reliably detected by GPC, indicating that a fraction of the unresolved oligomers (usually $n >$ ca. 6–8) in the GPC trace were cyclic. An example of a MALDI–TOF mass spectrum is shown in Fig. 3. In this spectrum signals due to cyclics up to the 17-mer are apparent, corresponding to 221-membered rings, whereas in the GPC trace it is difficult to reliably assign any peaks above the octamer (see Fig. 1).

The oligomers derived from polymer (**3b**) were also cyclic, and for similar reasons to those discussed earlier, but in addition to the simple family of GPC peaks there were significant extra peaks due to the presence of 2.7% of a cyclic "dimer" and 0.9% of a cyclic "trimer" each of which contained one diethyleneglycol unit in place of an ethyleneglycol unit. This was confirmed by mass spectrometry (see Fig. 4). Analogous oligomers have been found in the cyclic oligomers derived from poly(ethylene terephthalate) [30,31]. They probably arise due to ether formation

between glycol moieties being brought about under the vigorous polymerisation conditions in the presence of acidic catalysts.

Having established that the CDP products are families of cyclic oligomers, the question remains as to whether the first oligomer in an observed family is the cyclic monomer or dimer. In some cases it is readily apparent from molecular models that a cyclic monomer cannot be formed, but it is not clear when, as the ring sizes increase, it just becomes possible. To assist in such assignments three cyclic oligomers were isolated and characterised. These were the dimer (**17**) and monomers (**18**) and (**19**). With these cyclics clearly identified and the availability of data from such a closely related series of families, it was possible to confidently assign the starting points of the various cyclic oligomers families.

3.3. Conclusions to be drawn from the cyclo-depolymerisation results summarised in Table 3

Several conclusions can be drawn from the data in Table 3 and from related data.

First, the CDP of several polymers were carried out more than once by using different procedures. The two entries for the CDP of polymer (**7**) are typical of the results obtained. They show that the compositions of the cyclic oligomer fractions are essentially reproducible, with the yields of the major products being within ±3%. The entries for the CDP of polymer (**3b**) are atypical because the cyclic dimer
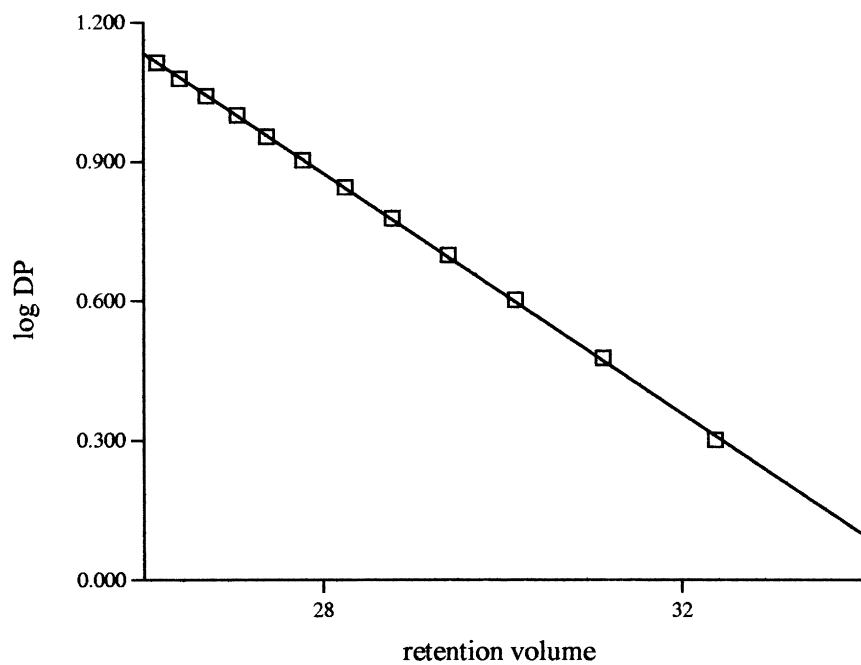
Fig. 2. Plot of the "retention volumes" vs. "log $\overline{DP}$" for the cyclic oligo(hexylidene isophthalate)s, from the GPC trace shown in Fig. 1.
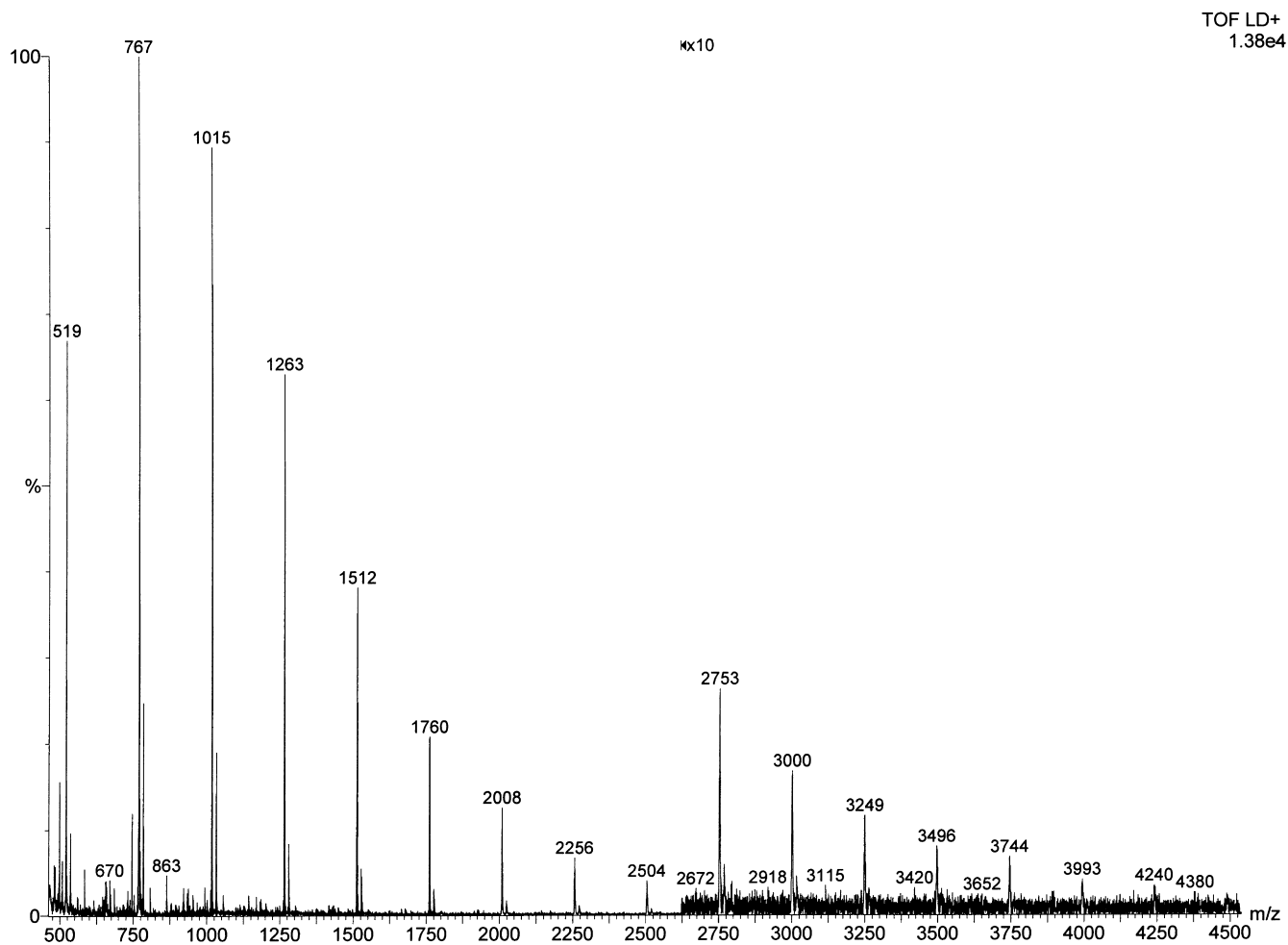

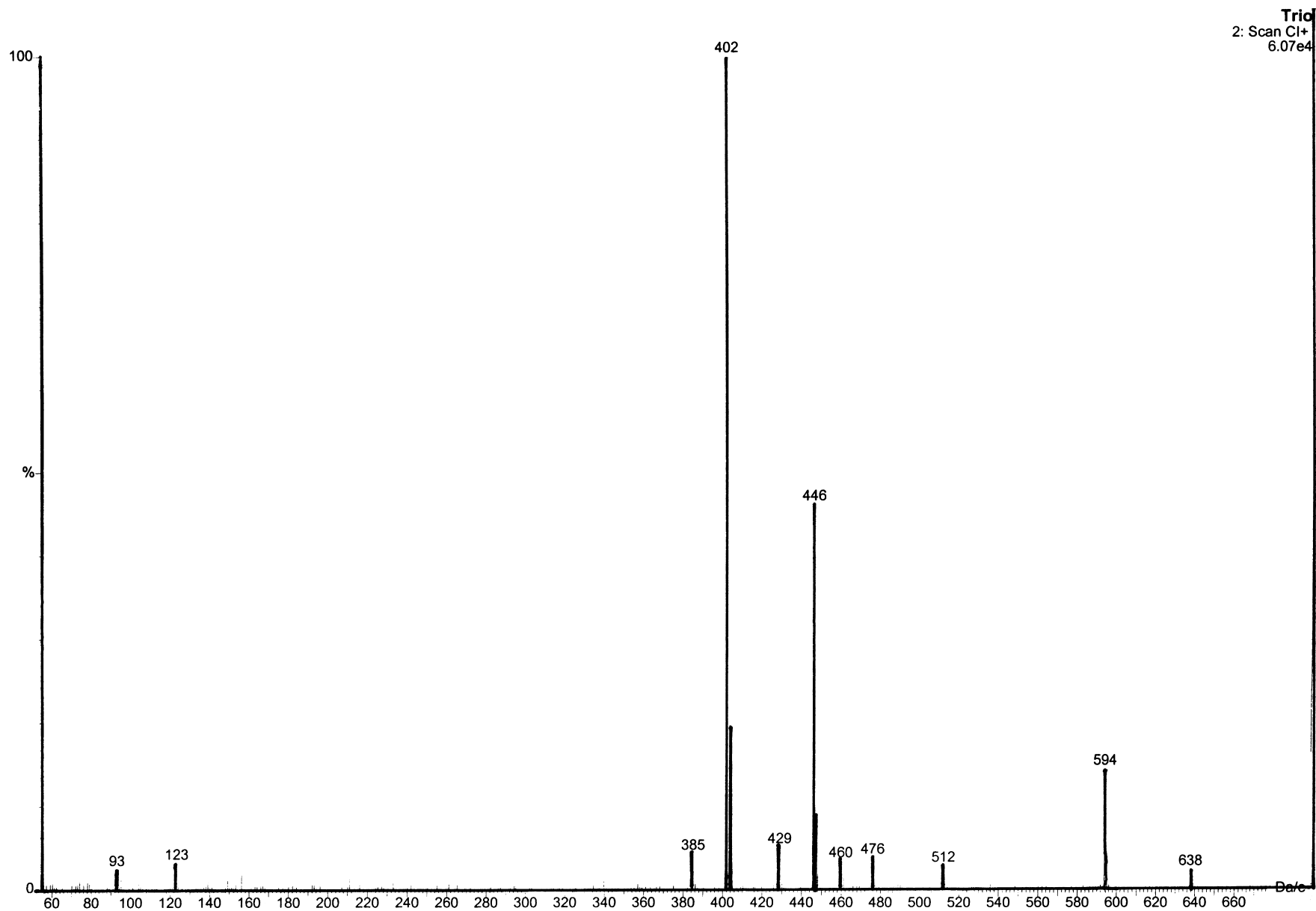Fig. 3. MALDI–TOF mass spectrum of the cyclic oligo(hexylidene isophthate)s formed by the CDP of linear polymer (**7**).

Fig. 4. CI mass spectrum of the CDP products from polymer (**3b**) showing the presence of cyclic dimer at $m/z = 402$ [(M + NH$_4$)$^+$] and trimer at $m/z = 594$, with further peaks 44 mass units higher, i.e. at $m/z = 446$ and 638, due to the presence of diethylene glycol units.
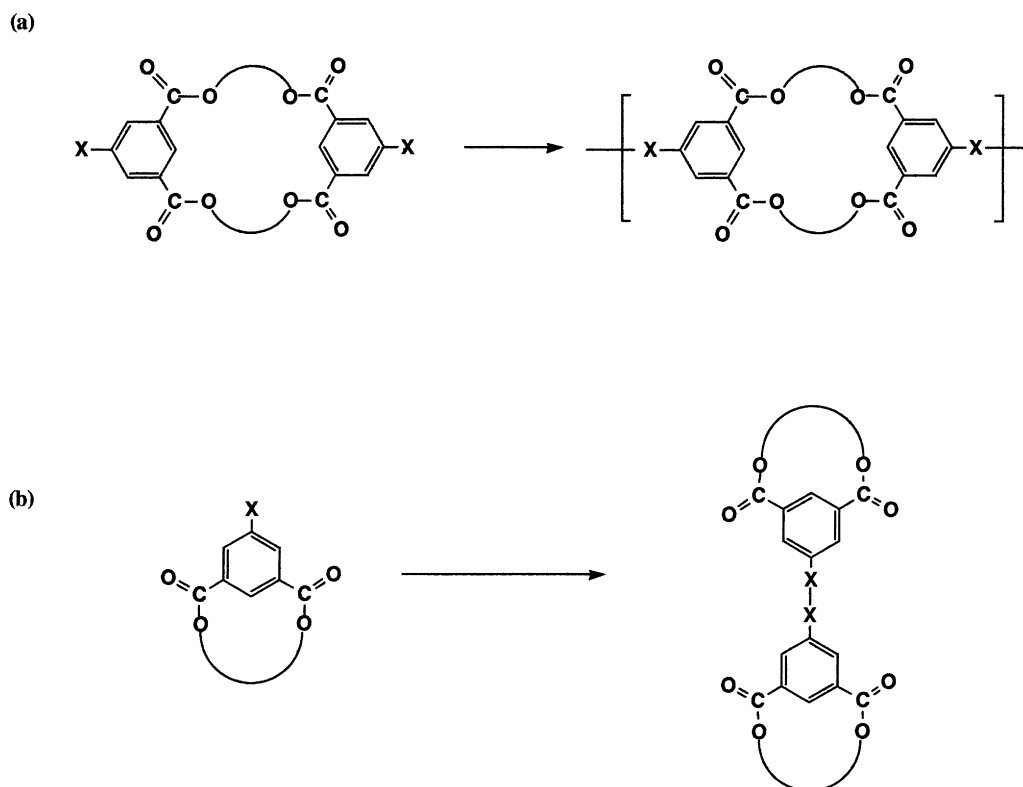
(a)

(b)

Fig. 5. Possible reactions involving the linking of functionalised cyclic oligomers: (a) conversion of cyclic dimer to a linear polymer; and (b) conversion of cyclic monomer to a crosslinking agent for ED-ROP.

tended to precipitate out during the reaction, hence frustrating the establishment of an equilibrium in solution.

Second, in several cases cyclics were formed with the same number of ring atoms per repeat unit both from polymers with simple hydrocarbon spacer units and from polymers with oligo(ethylene glycol) spacer units. Thus, the pairs of polymers **6** and **14**, **9** and **15**, and **12** and **16** produced families of cyclic oligomers with 12-, 15- and 18-ring atoms per repeat unit, respectively. In these cases the compositions of the cyclic oligomers fractions obtained from each pair were very similar and the yields of the major products were within ±5%, showing that the effect of replacing a methylene by an oxygen is small.

Third, similar cyclic oligomer mixtures to those obtained from polymers (**3b**), (**5b**), (**7**) and (**14**) have also been prepared recently by Brunelle et al. [9]. The compositions of our products and theirs differed considerably. However, Brunelle et al. synthesised their products by a novel pseudo-high dilution technique and the composition of the products were therefore determined by the relative rates at which each cyclic formed and not by its thermodynamic stability. Semlyen et al. have recently reported the CDP of polymers (**11**) and (**16**) [32]. The compositions of their products and ours differed significantly, in particular our products contained a much higher proportion of the cyclic monomer. It is, however, not clear from their report how

long the CDP reactions were carried out and hence whether or not they had thermodynamic products.

Fourth, all the products of the present CDP are potential feedstocks for ED-ROP and such studies are in hand.

Fifth, no cyclic monomer is present in the products from the CDPs of polymers (**3**)–(**8**) and the cyclic dimers were the major products. The cyclics have from 9 to 14 ring atoms per repeat unit. Functionalised derivatives of the cyclic dimers could be used as bifunctional monomers in step growth polymerisations to give linears with macrocyclic repeat units containing up to 28 ring atoms (see Fig. 5(a)).

Sixth, cyclic monomers were the major products from polymers with repeat units with more than 16 chain atoms, i.e. polymers (**10**)–(**13**) and (**16**). Functionalised derivatives of these cyclic monomers could be linked together and used as crosslinking agents in ED-ROP (see Fig. 5(b)).

Seventh, functionalised derivatives of the cyclic families from the CDP of polymers (**3**)–(**9**) would have an average functionality of >2 and could be used to form novel network materials.

Finally, all of the cyclic products from the CDPs of polymers (**6**)–(**8**) and (**14**) and the major products from polymers (**9**) and (**15**) have the potential to be threaded to afford polyrotaxanes [13]. This requires macrocycles with at least 22 ring atoms.

4. Conclusions

The synthesis of series of cyclic oligo(alkylidene isophthalate)s by the CDP of the corresponding linear polymers has been investigated and the yields of the various cyclic oligomers determined as a function of the polymer structure. With up to 15 ring atoms per repeat unit the main products are the cyclic dimers with smaller amounts of the larger rings. When there are more than 16 ring atoms per repeat unit the main products are the cyclic monomers with smaller amounts of the larger rings. Possible applications for such cyclic oligomers are discussed including their possible use as feedstocks for ED-ROP and as building blocks for novel polymeric structures.

Acknowledgements

References

[1] Semlyen JA, editor. Cyclic polymers. New York: Elsevier, 1986.
[2] Maravigna P, Montaudo G. Comprehensive polymer science, 5. Oxford: Pergamon, 1988 chap. 5, p. 63–90.
[3] Fawcett AH, Mee RAW, McBride FW. Macromolecules 1995;28:1481.
[4] Brunelle DJ. In: Ebdon JR, Eastmond GC, editors. New methods of polymer synthesis. London: Blackie, 1995.
[5] Hodge P, Colquhoun HM, Williams DJ. Chem Ind (London) 1998:162.
[6] Hall AJ, Hodge P. Reactive Polym 1999;39 in press.
[7] Goodman I, Nesbitt BF. Polymer 1960;1:384.
[8] Brunelle DJ, Shannon TG. Macromolecules 1991;24:3035.
[9] Brunelle DJ, Bradt JE, Serth-Guzzo J, Takekoshi T, Evans TL, Pearce EJ, Wilson PR. Macromolecules 1998;31:4782.
[10] Diederich F. Cyclophanes. Cambridge: Royal Society of Chemistry, 1991.
[11] Cram DJ, Cram JM. Container molecules and their guests. Cambridge: Royal Society of Chemistry, 1994.
[12] Gokel GW. Crown ethers and cryptands. Cambridge: Royal Society of Chemistry, 1991.
[13] Gibson HW, Gong C, Liu S, Nagvekar D. Macromol Symp 1998;128:89 and references therein.
[14] Wang YF, Hay AS. Macromolecules 1996;29:5050.
[15] Teasley MF, Wu DQ, Harlow RL. Macromolecules 1998;31:2064.
[16] Baxter I, Colquhoun HM, Hodge P, Kohnke F, Williams DJ. Chem Comm 1998:283.
[17] Chen M, Gibson HW. Macromolecules 1996;29:5502.
[18] Xie D, Ji Q, Gibson HW. Macromolecules 1997;30:4814.
[19] Peng P-P, Hodge P. Polymer 1998;39:981.
[20] Hodge P, Peng P-P. Polymer 1999;40:1871.
[21] Fridkin M, Patchornik A, Katchalski E. J Am Chem Soc 1965;87:4646.
[22] Rothe M, Lohmuller M, Breuksch U, Schmidtberg G. Angew Chem Indl Edn 1994;33:1960.
[23] Hodge P, Houghton MP, Lee MSK. J Chem Soc Chem Comm 1993:581.
[24] Rothe M, Zieger M. Tet Let 1994;35:9011.
[25] Nelissen M, Keul H, Höcker H. Macromol Chem Phys 1995;196:1645.
[26] Brunelle DJ, Takekoshi T. US Patent, 1995, No. 5 407 984.
[27] Hubbard PA, Brittain WJ, Mattice WL, Brunelle DJ. Macromolecules 1998;31:1518.
[28] Wood BR, Semlyen JA, Hodge P. Polymer 1997;38:191.
[29] Wood BR, Semlyen JA, Hodge P. Polymer 1997;38:2287.
[30] Bryant JJ L, Semlyen JA. Polymer 1997;38:2475.
[31] Bryant JJL, Semlyen JA. Polymer 1997;38:4531.
[32] Hamilton SC, Semlyen JA, Haddleton DM. Polymer 1998;39:3241.
[33] Baxter I, Ben-Haida A, Colquhoun HM, Hodge P, Kohnke FH, Williams DJ. Chem Comm 1997:1533.
[34] Baxter I, Ben-Haida A, Colquhoun HM, Hodge P, Kohnke FH, Williams DJ. Chem Comm 1997:2213.
[35] Hodge P, O'Dell R, Lee MSK, Ebdon JR. Polymer 1996;37:1267 and references therein.
[36] Berr CE. J Polym Sci 1955;15:591.
[37] Bradshaw JS, Thompson MD. J Org Chem 1978;43:2456.
[38] Semlyen JA. Adv Pol Sci 1976;21:41.
[39] Jacobson H, Stockmayer WH. J Chem Phys 1950;18:1600.