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Cyclo-depolymerisation of poly(ethylene naphthalene-2,6-dicarboxylate) and ring-opening polymerisations of the cyclic oligomers obtained

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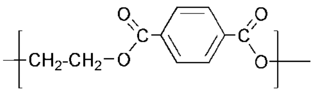
Commercial poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) was cyclo-depolymerised by treatment of a suspension in 1,2-dichlorobenzene at 180 °C with 3 mol% of di-*n*-butyltin oxide as a catalyst. The cyclic oligomers, produced in up to 93% yield, were characterised by gel permeation chromatography, ^{1}H NMR spectroscopy and mass spectrometry. The products contained cyclic oligomers ranging from the dimer up to at least the nonamer, with the trimer being the most abundant. Careful column chromatography of the mixture allowed pure samples of the cyclic trimer and tetramer to be isolated. Ring-opening polymerisation of the mixture of cyclic oligomers could be achieved by heating the mixture with a catalytic amount of di-*n*-butyltin oxide at 350 °C for 10 min. These interconversions of PEN and the corresponding cyclic oligomers form the basis of a potential method to recycle this valuable commercial polymer. Cyclic oligomers were similarly prepared from commercial poly(ethylene terephthalate) (PET) and these were then homopolymerised and copolymerised with the cyclic oligomers from PEN.

Introduction

For statistical reasons[1–3] the products of step-growth polymerisations generally contain a small cyclic fraction, which typically is $<2\%$ of the mass. This results from chain ends reacting *intramolecularly* rather than *intermolecularly* during the polymerisation. As a consequence a wide range of cyclic oligomers has been known for many years.[4–6] The presence of the cyclic oligomers is sometimes a cause for concern as they may, for example, modify the mechanical properties of the product by plasticising it. Recently, however, there has been an increased interest in the cyclic oligomers. It has been recognised that they can serve as feedstocks for a novel type of ring-opening polymerisation (ROP) which is environmentally friendly.[7–9] In this type of ROP a *neat* sample of cyclic oligomers is treated with a catalyst under conditions that result in the reversible breakage of the linkages between the monomer units. Under the *high concentration* conditions polymer is formed by an entropically driven (ED) process during which there is neither evolution of volatiles nor major evolution of heat. To make this ED-ROP process useful it is clearly necessary to have a very good source of the appropriate cyclic oligomers. One source of considerable interest is from the cyclo-depolymerisation (CDP) of the corresponding linear polymer, because used in combination with ED-ROP it provides a possible means of recycling many step-growth polymers.

For CDP, reaction conditions are again chosen so that the linkages joining the polymer repeat units are repeatedly broken and then re-formed. In contrast to the ED-ROP reaction, however, CDP is carried out at *high dilution*. The reaction then affords cyclic oligomers in good yield. Whilst such ring–chain interconversions are well known,[1,2,10] 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 been synthesised by CDP under high dilution conditions. These include polycaprolactone,[11] polyoctanoate,[12] polydecanoate,[12] polyundecanoate,[12] polydodecanoate,[12] poly(ethylene terephthalate) (PET) (**1**),[13] poly(butylene terephthalate),[14,15] poly(decamethylene terephthalate),[16] poly[tetra(ethylene glycol) terephthalate],[17] poly[tetra(ethylene glycol) succinate][18] and a wide range of poly(alkylidene isophthalate)s.[19] Spanagel and Carothers have described the CDP of polydecanoate, polytridecanoate and polytetradecanoate by simply heating them under vacuum at 270 °C in the presence of magnesium chloride and collecting the distillate.[20] Under these conditions the potential ring–chain equilibria are displaced by



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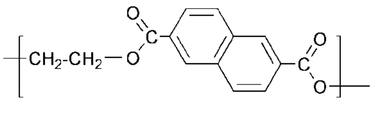

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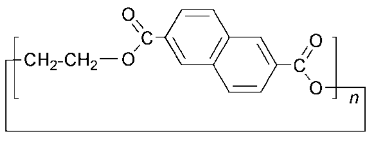
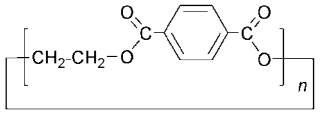


3 : $n = 2$ to >9
3a : $n = 3$
3b : $n = 4$



4 : $n = 3$ to >12

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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. More recently polycaprolactone has been similarly converted into cyclic oligomers.[11]

This paper describes the CDP of a further polyester, namely poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) (**2**), a commercial polymer currently of interest because many of its properties are superior to those of PET (**1**), the characterisation of the cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (**3**) so obtained, the isolation and characterisation of the cyclic trimer (**3a**) and tetramer (**3b**), the ED-ROP of the mixture of cyclic oligomers (**3**) and of the cyclic trimer (**3a**), and the copolymerisation of the mixture (**3**) with the mixture of cyclic oligomers (**4**) obtained by the CDP of PET (**1**).[13] The CDP of PEN (**2**) has been referred to in a patent but no specific details were given.[21] Cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (**3**) have recently been synthesised *directly* from the diacid chloride of naphthalene-2,6-dicarboxylic acid and ethylene glycol under high dilution conditions, and the ROP of the cyclic oligomers was briefly investigated.[22]

Results and discussion

Synthesis and characterisation of cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (3)

PEN (**2**) has a very low solubility in the common solvents which may be suitable for CDP, so it was difficult *a priori* to select suitable conditions for the reaction. Accordingly a range of reaction conditions was investigated using several different catalysts and solvents. Initially reactions were carried out using 3 mol% of three different catalysts and suspensions of the polymer in 1,2-dichlorobenzene heated under reflux: see Table 1, entries 1–3. All the reactions were sluggish. That using bis(tributyltin) oxide gave the best yield of soluble products (see entry 1) but analysis by gel permeation chromatography (GPC) indicated that the mixture was very complex, possibly because soluble linear products with tributyltin end groups were formed. Dibutoxydibutyltin was a very effective catalyst for the CDP of polyundecanoate,[12] but was not in the present case: see entry 2. Although the use of dibutyltin oxide (DBTO) gave a modest yield, the soluble products were essentially pure cyclic oligomers (**3**): see entry 3. Other solvents, namely DMSO and α-methylnaphthalene at their reflux temperatures, were tried with DBTO as the catalyst but the yields of soluble products after 7 days were < 10%. Thus, the best catalyst–solvent combination was DBTO in 1,2-dichlorobenzene. A much improved yield of cyclic oligomers was then obtained using this combination but with the PEN (**2**) finely milled: see entry 4. After 3 days the yield of clean oligomers (**3**) was now 93%. Only products prepared in this way were studied further.

The cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (**3**) were characterised using various methods. The infrared spectrum showed a single sharp carbonyl band at 1722 cm^{-1} and the ^1H NMR spectrum showed just one strong singlet at δ 4.80 in the region where signals due to CH_2O are expected, *i.e.* there was no evidence for end groups. The most detailed analysis of the cyclic oligomers was achieved by GPC. As expected many oligomers were produced: see Fig. 1. A plot of 'log DP_n' *versus* 'Retention Volume' was a straight line, see Fig. 2, so confirming that the peaks were all due to oligomers of one series which, in view of the spectroscopic data given above, was clearly a series of cyclics. The amount of each cyclic present was as summarised in Table 1. The main component, up to 68% by weight, was the cyclic trimer (**3a**) and, as expected from the theory of Jacobson and Stockmeyer,[23] the larger oligomers were then present in amounts which decreased progressively as the rings became larger. Under the best GPC conditions cyclic oligomers from the dimer up to the nonamer (108 ring atoms) were detected. The amounts of the individual cyclic oligomers obtained here, essentially under thermodynamic control, differ considerably from those reported by Brittain *et al.*,[22] who prepared them directly, under kinetic control, from the diacid chloride and ethylene glycol under high dilution conditions. They obtained species ranging from the cyclic dimer to the

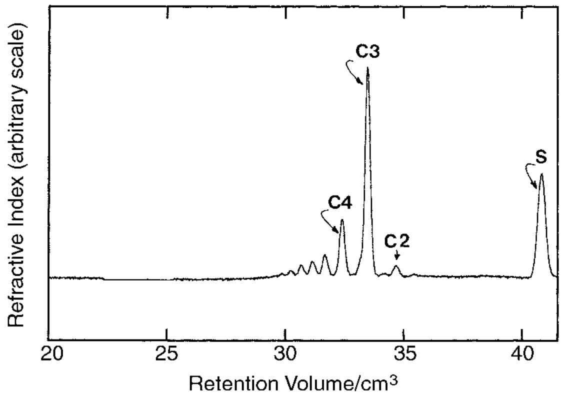


Fig. 1 GPC trace of cyclic oligomers (**3**) obtained by the CDP summarised in Table 1, entry 3. S = standard.

Table 1 Cyclo-depolymerisations of PEN (**3**)[a] and PET (**1**)[b]

							Composition of soluble product[d]							
		Reaction conditions[c]					Percentage yield of cycle *n*-mers by weight							
Entry	Starting polymer	Concentration (w/v)	Catalyst	*t*/h	Yield of soluble product	Ring atoms per repeat unit	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n \geqslant 8$[e]	MALDI-TOF MS[f]
1	PEN (**2**)	2.0	A	240	78	12	[g]	[g]	[g]	[g]	[g]	[g]	[g]	—
2	PEN (**2**)	2.0	B	240	7	12	—	—	—	—	—	—	—	—
3	PEN (**2**)	2.0	C	240	43	12	3	62	16	7	4	3	1[h]	9
4	PEN (**2**)[i]	1.3	C	72	93	12	2	68	14	6	3	2	1[h]	9
5	PET (**1**)	2.5	D	48	80	10	2	70	7	5	4	2	5[j]	—
6	PET (**1**)	2.5	C	48	82	10	2	66	7	6	5	3	6[j]	12

[a] Poly(ethylene naphthalene-2,6-dicarboxylate) (**2**). See Experimental section for source and inherent viscosity data. [b] Poly(ethylene terephthalate) (**1**). See Experimental section for source and inherent viscosity data. [c] All reactions were carried out in 1,2-dichlorobenzene at reflux temperature (*ca.* 180 °C) and used 3 mol% of catalyst. Catalyst A = $(n\text{-}C_4H_9)_3SnOSn(n\text{-}C_4H_9)_3$; Catalyst B = $(n\text{-}C_4H_9)_2Sn(O\text{-}n\text{-}C_4H_9)_2$; Catalyst C = $(n\text{-}C_4H_9)_2SnO$; and Catalyst D = $(n\text{-}C_4H_9)_2Sn(OCH_2CH_2O)_2Sn(n\text{-}C_4H_9)_2$ (**5**). [d] By GPC analysis. [e] These values include mainly unidentified higher cyclic oligomers. [f] Peaks due to cyclics were clearly seen from $n = 3$ up to the values given. [g] Complex, poorly resolved mixture with many components that were not cyclic oligomers. [h] Plus 4% of cyclic oligomers presumed to be those incorporating di(ethylene glycol) units. [i] The polymer was milled prior to carrying out the reaction. [j] Plus 5% of cyclic oligomers incorporating some di(ethylene glycol) units.

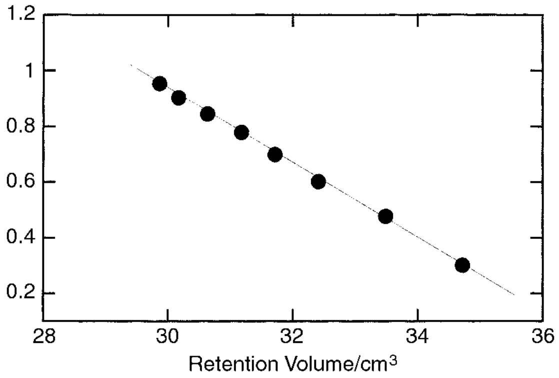


Fig. 2 Plot of 'log DP' *versus* 'Retention Volume' for oligomers produced in the experiment summarised in Table 1, entry 3.

cyclic pentamer in yields of 19, 34, 27 and 20%, respectively. The most notable difference is that obtained for the dimer: 3% by CDP in the present work *versus* 19% by the direct synthesis. In order to confirm our assignments in the GPC traces we sought to isolate and characterise at least one cyclic oligomer. Careful column chromatography of the cyclic oligomers (**3**) afforded pure samples of both the cyclic trimer (**3a**) and the cyclic tetramer (**3b**). These were characterised using standard methods and were used to confirm our GPC peak assignments.

The MALDI-TOF mass spectrum of the cyclic product (doped with Li^+ cations in the form of LiBr) confirmed the presence of rings from the cyclic trimer up to the cyclic 11-mer: see Fig. 3. For each cyclic there was a strong $[M+Li]^+$ peak. In addition to these peaks, in each case there were much smaller peaks at $M^+ + 44$ and $M^+ + 88$ which can be attributed to the presence of cyclic oligomers with one or two di(ethylene glycol) units in place of ethylene glycol units. For example, for the pentamer there were peaks at 1217, 1261 and 1305. Such units are known to be present up to a level of *ca.* 5% in PET (**1**) and to be formed under the vigorous conditions used bring about the original melt polymerisation.[13] As expected, they were not reported to be present in the cyclic oligomers (**3**) produced by the reaction of the diacid chloride of 2,6-dinaphthoic acid with ethylene glycol under high dilution conditions.[22]

Synthesis and characterisation of cyclic oligo(ethylene terephthalate)s (4)

Cyclic oligo(ethylene terephthalate)s (**4**) have been prepared before by the CDP of PET (1).[13] They were required in the present work as monomers for use in ED-ROPs (see below) and were successfully prepared from PET (**1**) using a similar procedure to that used with PEN (**2**). The results are summarised in Table 1, entries 5 and 6. The cyclic fractions were characterised by means of GPC, ^1H NMR and MALDI-TOF mass spectrometry.

Ring-opening polymerisations using cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (3)

As noted in the Introduction, cyclic oligomers are currently of interest as feedstocks for ED-ROP. Two approaches were used for carrying out ED-ROP in the present work. In Method I pellets of the mixture of cyclic oligomers (**3**) or of the pure cyclic trimer (**3a**) with 3.0 mol% of DBTO as the catalyst were heated in a DSC apparatus at 350 °C for 10 min. In order to give the ED-ROPs the opportunity to proceed to completion, the reaction temperature selected was above the T_m (261 °C) of PEN (**2**). In Method II a mixture of the cyclic oligomers (**3**) with 0.2 mol% of titanium tetraisopropoxide as the catalyst was cast as a film on a microscope slide using chloroform. The film was then heated at 265 °C in a vacuum for 24 h. Table 2 summarises the results. In all cases polymerisation occurred and the products had T_g and/or T_m values close to those of the original PEN (**2**). Method II produced self-standing films, so demonstrating the potential use of ED-ROP to prepare coatings. The products obtained using Method I were discoloured; the products from Method II much less so. The inherent viscosities of the products produced by Method I were measured and found to have significant values but they were only 63% (entry 1) and 86% (entry 3) of the values of the starting polymer. In the work of Brittain *et al.* the ED-ROPs were carried out at 295–300 °C for 25 min using 1 mol% of titanium tetraisopropoxide as catalyst. As in our work the T_m of the product agreed well with that expected for PEN (**2**), but the inherent viscosity was only 48% that of their starting polymer.

PET (**1**) is used in a wide variety of industrial applications.

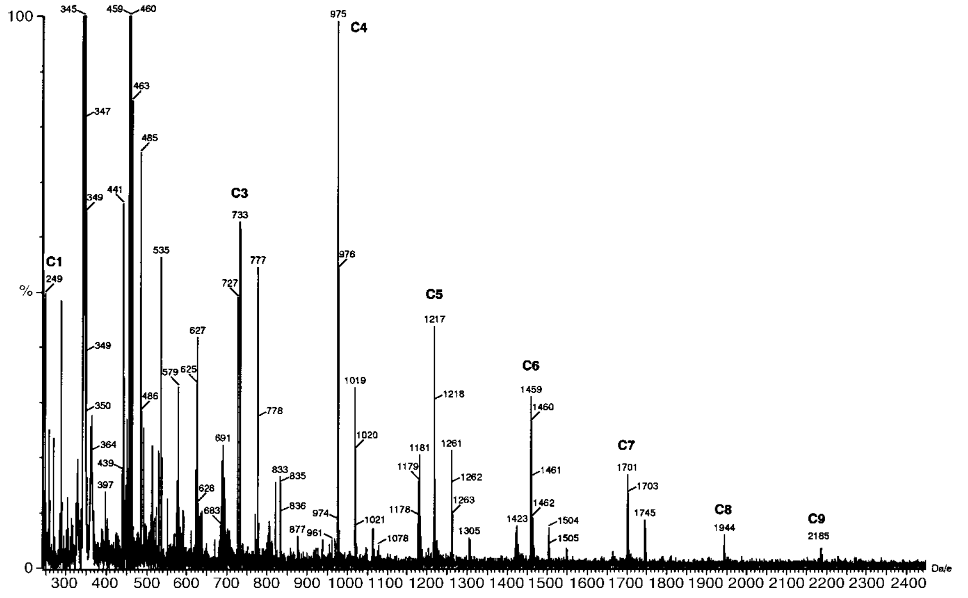


Fig. 3 MALDI-TOF mass spectrum of cyclic oligomers (**3**) obtained by the CDP experiment summarised in Table 1, entry 3. Sample doped with lithium bromide.

Table 2 Ring-opening polymerisations of various samples and selected properties of the products

		Ring-opening polymerisation conditions[a]					Properties of product		
Entry	Starting material	Form of cyclic oligomer sample	Catalyst[b]	Catalyst/mol%	T/°C	t/min	Inherent viscosity	T_g/°C	T_m/°C
1	Cyclic oligomers (**3**)[c]	Pellet	C	3.0	350	10	0.35[d]	120	261
2	Cyclic oligomers (**3**)[e]	Cast film[f]	E	0.2	260	1440	—	118	[g]
3	Cyclic trimer (**3a**)	Pellet	C	3.0	350	10	0.48[d]	119	263
4	Cyclic oligomers (**4**)	Pellet	D	0.2	280	60	0.55[h] (0.73[h])[i]	75	250
5	Cyclic oligomers (**4**)	Cast film[f]	D	0.2	265	60	0.40[h]	—	255
6	A 50 : 50 (w/w) mixture of cyclic oligomers (**3**)[c] and (**4**)[k]	Pellet	C	3.0	350	10	0.44[h]	99	315[j]

[a]All reactions carried out under a nitrogen atmosphere. [b]Catalyst C = $(n\text{-}C_4H_9)_2SnO$; Catalyst D = $(n\text{-}C_4H_9)_2Sn(OCH_2CH_2O)_2Sn(n\text{-}C_4H_9)_2$; and Catalyst E = titanium tetraisopropoxide. [c]Cyclic oligomers produced from the reaction summarised in Table 1, entry 4. [d]For a 0.1% solution in concentrated H_2SO_4. [e]Cyclic oligomers produced from the reaction summarised in Table 1, entry 3. [f]Cast from a solution in chloroform onto a microscope slide. [g]Temperature only taken up to 210 °C. [h]For a 0.1% solution in trifluoroacetic acid. [i]Viscosity after extracting the product with chloroform. The extraction decreased the sample weight by 5%. [j]Compared with the T_m peak of the PEN (**2**) products, this peak was very small. The sample was substantially amorphous. [k]Cyclic oligomers produced from the reaction summarised in Table 1, entry 6.

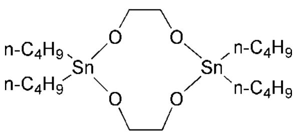
PEN (**2**) has superior properties but is much more expensive. This has prompted the synthesis of copolymers *via* transesterification reactions in blends.[24] It was considered of interest to prepare a copolymer by carrying out an ED-ROP with a mixture of cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (**3**) and cyclic oligo(ethylene terephthalate)s (**4**). The preparation of the cyclic oligomers (**4**) from PET was considered above. The ROP of cyclic oligomers (**4**) has been studied previously by Goodman and Nesbitt using antimony oxide as a catalyst.[25] Prior to carrying out the planned copolymerisation, the cyclic oligomers (**4**) were homopolymerised using both Methods I and II with the distannoxane (**5**) as the catalyst: see Table 2, entries 4 and 5. Both methods gave products with T_ms close to that of PET (**1**), but the pellet method gave the product with the higher inherent viscosity; 82% that of the starting polymer. However, washing the product with chloroform to remove oligomers afforded a sample (95% of the original weight) with an inherent viscosity of 0.73, *i.e.* 9% higher than the original commercial polymer sample. The presence of some oligomers in the ED-ROP product is not surprising since establishing the ring–chain equilibrium even at high concentration will always mean there are some cyclic oligomers present. Having demonstrated that the homopolymerisation proceeds smoothly, a copolymerisation was then carried out using a 50 : 50 w/w mixture of cyclic oligomers (**3**) and (**4**): see Table 2 entry 6. The product had a significant inherent viscosity, displayed a T_g of 99 °C, *i.e.* different from and between the values for the two homopolymers. It was almost entirely amorphous.

Conclusions

The cyclo-depolymerisation of linear PEN (**2**) has been studied in some detail. Reaction conditions were identified that allow the cyclic oligomers (**3**) to be obtained in high yield. The oligomers were characterised by GPC, ^1H NMR spectroscopy and mass spectroscopy. The cyclic trimer (**3a**) and cyclic tetramer (**3b**) were isolated and characterised. The cyclic oligo(ethylene naphthalene-2,6-dicarboxylate)s (**3**) successfully under went ED-ROP to afford PEN (**2**). Cyclic oligo(ethylene terephthalate)s (**4**) were similarly prepared from PET (**1**). These were both homopolymerised and copolymerised with the cyclic oligomers (**3**) from PEN (**2**).

Experimental

All reagents were used as purchased. Bis(tri-*n*-butyltin)oxide, di-*n*-butoxydibutyltin, di-*n*-butyltin oxide (DBTO) and titanium tetraisopropoxide were purchased from Aldrich. Dioxastannoxane (**5**) was prepared by the literature method.[21,26]



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Details of general experimental procedures and the instruments used for analyses are as given previously.[12]

Source and properties of PEN (2) and PET (1)

The sample of PEN (**2**) was purchased from Aldrich, UK. It was in the form of pellets (size *ca.* 2 × 2 × 4 mm). A 0.1% solution in concentrated sulfuric acid at 20 °C had an inherent viscosity 0.56 dL g^{-1}. It had T_g = 119 °C (lit.,[5] 113 °C) and T_m = 261 °C (lit.,[5] 260 °C). A sample was extracted with dioxane for 10 days using a Soxhlet apparatus. Evaporation of the solvent afforded an oily residue (0.5% w/w) which, by GPC analysis, contained no cyclic oligomers. A similar result was obtained when chloroform was used for the extraction.

The sample of PET (**1**) was purchased from Scientific Polymer Products, New York. It was in the form of pellets (*ca.* 2 × 3 × 4 mm). A 0.1% solution in trifluoroacetic acid at 20 °C had an inherent viscosity of 0.67 dL g^{-1}. It had T_g = 79 ° (lit.,[5] 69 °C) and T_m = 255 °C (lit.,[5] 250–265 °C, depending on the content of di[ethylene glycol] units).

Cyclo-depolymerisation reactions

The experiments are summarised in Table 1. The PEN (**2**) and PET (**1**) were used as received, except in the case of the experiment summarised in entry 4, when the PEN (**2**) pellets were milled to give a 50 μm diameter powder. The procedures used in the following experiments are typical.

Entry 4: cyclo-depolymerisation of PEN (2). A suspension of milled PEN (**2**) (2.00 g, 8.26 mmol) in 1,2-dichlorobenzene (150 ml) containing DBTO (62 mg, 0.25 mmol, 3 mol%) was vigorously stirred and heated under reflux. After 24 h the reaction mixture was homogeneous. Heating was continued for a further 48 h. The mixture was cooled to ambient temperature and filtered then, to minimise the possibility of the equilibrium being shifted, the solvent was rapidly evaporated off at 50 °C and 1.0 mmHg. The recovered solid was suspended for 30 min in methanol (60 ml) at 50 °C. The product was then collected, washed with methanol and dried in a vacuum oven (60 °C, 0.3 mmHg). The product (1.85 g, 93%) had ν_{max} (KBr disk) 1722 cm^{-1}; δ_H 4.80 (s; relative integral 4H; -CH_2-O), 7.95 (m;

2H; 4- and 8-H on naphthalene ring), 8.10 (m; 2H; protons at 3- and 7-positions of naphthalene ring), and 8.62 (m; 2H; protons at 1- and 5-positions of naphthalene ring). The results of the GPC analysis are summarised in Table 1. The MALDI-TOF mass spectrum is shown in Fig. 3.

Entry 6: cyclo-depolymerisation of PET (1). A suspension of PET (**1**) (3.00 g, 15.63 mmol) in 1,2-dichlorobenzene (120 ml) containing DBTO (120 mg, 0.48 mmol, 3 mol%) was vigorously stirred and heated under reflux for 48 h. The mixture was then cooled to 75 °C and the insoluble material filtered off (0.54 g, 18%). The filtrate was rapidly evaporated to dryness at 80 °C and 1.0 mmHg. The residue (2.46 g, 82%) had ν_{max} (film) 1723 cm^{-1}; δ_H ($CDCl_3$) 4.70 (s; relative integral 4H; -CH_2O-) and 8.10 (s; 4H; aromatic-H). The results of the GPC and MALDI-TOF mass spectrum analyses are summarised in Table 1. The data are in excellent agreement with those reported in the literature.[13]

Isolation of cyclic trimer (3a) and cyclic tetramer (3b)

A portion (1.00 g) of the cyclic oligomers (**3**) fraction from the experiment summarised in Table 1, entry 4, was subjected to column chromatography over silica gel using dichloromethane–ethyl acetate (94 : 6 v/v) as the eluent. This afforded the trimer (**3a**) and tetramer (**3b**).

Cyclic trimer (3a). (590 mg, 59%), recrystallised from a mixture of dichloromethane and methanol, had mp 369 °C (by DSC); ν_{max} (KBr disk) 1723 cm^{-1}; FAB-MS using mNBA, 726 [M^+, 100%]; δ_H ($CDCl_3$) 4.83 (s; relative integral 4H; -CH_2O-), 8.00 (d; $J = 8.5$ Hz; 2H; protons at 4- and 8-positions of naphthalene ring), 8.14 (dd; $J = 1.5$ and 8.5 Hz; 2H; protons at 3- and 7-positions of naphthalene ring) and 8.65 (d; $J = 1.5$ Hz; 2H; protons of 1- and 5-positions of naphthalene ring); δ_C ($CDCl_3$) 62.72 (-CH_2O-), 125.90, 129.16, 129.71 and 130.71 (carbons at 1-, 3-, 4-, 4a-, 5-, 7-, 8-, and 8a- positions of naphthalene nucleus), 134.55 (carbons at positions 2- and 6- positions of naphthalene nucleus) and 165.91 (carbonyls). Found: C, 69.42; H, 4.43%. Calculated for $(C_{14}H_{10}O_4)_3$ C, 69.42; H, 4.13%.

Cyclic tetramer (3b). (90 mg, 9%), recrystallised from a mixture of dichloromethane and methanol, had mp 331 °C; ν_{max} (KBr disk) 1722 cm^{-1}; MALDI-TOF MS using dithranol, 991 ($[M+23]^+$; 100%); δ_H ($CDCl_3$ plus 5% v/v CF_3CO_2H) 4.78 (s; relative integral 4H; -CH_2O-), 7.92 (d; $J = 8.5$ Hz; 2H; protons at 4- and 8-positions of naphthalene ring), 8.02 (dd; $J = 1.5$ and 8.5 Hz; 2H; protons at 3- and 7-positions of naphthalene ring) and 8.57 (d; $J = 1.5$ Hz; 2H; protons of 1- and 5-positions of naphthalene ring); δ_C ($CDCl_3$) 63.84 (-CH_2O-), 125.90, 128.66, 129.99 and 131.24 (carbons at 1-, 3-, 4-, 4a-, 5-, 7-, 8-, and 8a- positions of naphthalene nucleus), 134.72 (carbons at positions 2- and 6- positions of naphthalene nucleus and 167.62 (carbonyls). Found: C, 69.18; H, 4.65%. Calculated for $(C_{14}H_{10}O_4)_4$ C, 69.42; H, 4.13%.

Ring-opening polymerisations of cyclic oligomers

The following experiments are typical of those summarised in Table 2.

Entry 1: polymerisation of the mixture of cyclic oligomers (3). The cyclic oligomers (**3**) (110 mg, 0.45 mmol) were mixed in a pear-shaped flask with DBTO (3.5 mg, 14.3 mmol, 3 mol%) in tetrahydrofuran (9 ml). The mixture was thoroughly stirred and sonicated for 1 h. The solvent was evaporated *in vacuo*, and the sample was dried overnight in a vacuum oven at 40 °C. A portion of the sample (20 mg) was pressed into a pellet and heated at 350 °C for 10 min in a DSC under nitrogen. The sample was cooled to 30 °C and then scanned to 350 °C at a rate of 10 °C min^{-1}. The DSC thermogram showed a T_g at 120 °C and a T_m at 261 °C. The product was a hard yellow glass. A 0.1% solution of the product in conc. sulfuric acid had an inherent viscosity of 0.35 dL g^{-1}.

Entry 5: polymerisation of cyclic oligomers (4). The cyclic oligomers (**4**) (25 mg) were dissolved in dichloromethane (2 ml) containing the tin catalyst (**5**) (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 vacuum oven (0.1 mmHg) and heated at 265 °C. After 60 min the plate was removed and allowed to cool to room temperature. The product could be peeled from the slide as a free standing-film. The product was very pale yellow. The polymer had an inherent viscosity of 0.40 dL g^{-1} in CF_3CO_2H. The results are summmarised in Table 2.

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