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Cyclic polyesters: 7. Preparation and characterization of cyclic oligomers from solution ring-chain reactions of poly(butylene terephthalate)

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Solution ring-chain reactions of poly(butylene terephthalate) (PBT) were carried out using 1,2-dichlorobenzene (b.p. 180°C) with a catalyst. By increasing the dilution to 1:70 (polymer/solvent ratio w/v), cyclic PBT oligomers were obtained in a yield of 70 wt%. This compares to cyclic oligomers of PBT extracted from commercial PBT chip using mixed xylene isomers, in a yield of 1 wt%. The cyclic oligomers produced in the solution ring-chain reaction and obtained from the extract were found to contain oligomers $(CO.C_6H_4CO.O.(CH_2)_4O)_x$, where $x = 2$–9. The cyclic oligomers of PBT were analysed using PL-gel mixed E gel permeation chromatographic columns, fast atom bombardment mass spectrometry and liquid chromatography tandem mass spectrometry. The cyclic dimer of PBT, $(CO.C_6H_4CO.O.(CH_2)_4O)_2$, was separated, purified and crystallized and its X-ray crystal structure determined. © 1997 Elsevier Science Ltd.

(Keywords: cyclic polyester; gel permeation chromatography; poly(butylene terephthalate))

INTRODUCTION

In a previous investigation[1] we reported how solution ring-chain reactions could be used to prepare a range of cyclics, $(CO.C_6H_4.CO.O.CH_2.CH_2.O)_x$ with $x = 3$–13, of the commercially important polymer, poly(ethylene terephthalate) (PET). There have been many previous studies reported in the chemical literature describing cyclic oligomers of PET extracted from samples of commercial PET[2–6]. However, in the case of PBT there are relatively few reported publications on cyclic PBT oligomers found in extracts from commercial samples, or indeed on preparative methods of cyclic oligomers of PBT.

Montaudo *et al.*[7] described the extraction of cyclic oligomers from PET and PBT samples, using the polymer dissolution method[8]. They also prepared cyclics of PET and PBT using melt equilibration reactions. Kitano *et al.*[9] described the X-ray crystal structure of the cyclic dimer of PBT after the cyclic oligomers had been extracted from a commercial sample of PBT. In an earlier investigation, East and Girshab[10] described extraction procedures for cyclic oligomers of PBT from samples of PBT chip, using two methods, by dissolution in *o*-dichlorobenzene and extraction of cyclic oligomers with chloroform, which yielded between 1.5 and 1.8% cyclic oligomers, and also by dissolving polymer in trifluoroacetic acid followed by precipitation (a method described by Hudgins *et al.*[11]), which yielded 1.5% cyclic oligomers. These cyclic oligomers were analysed by high performance liquid chromatography (h.p.l.c.) and thin layer chromatography (t.l.c.). East and Girshab compared the distribution of cyclic oligomers of PBT in their extracts with those reported by Burzin *et al.*[12] for the equilibrium amounts of cyclic dimer, trimer and tetramer, and they described briefly their own attempts at melt equilibrium reactions at 255°C. The cyclic content of the molten polymer was lowered when titanium tetraisopropoxide was used and they then commented on the possibility that the thermodynamic equilibrium had not been attained due to decomposition processes.

There is a growing interest in methods for making macrocyclic oligomers of commercially important polymers, such as cyclic polystyrene[13], cyclic poly(alkylene discarboxylate)[14,15], cyclic aryl ethers[16,17], cyclic polyimides[18] and cyclic polycarbonates[19,20], because these macrocyclic oligomers can be used for various processing technologies where the physical and chemical properties of the macrocyclic oligomers have advantages over the corresponding linear polymers.

This paper describes how we have prepared a range of cyclic oligomers of PBT in good yields using solution ring-chain reactions. The conditions necessary are described in detail. These cyclic oligomers of PBT are required for future work in our laboratory.

EXPERIMENTAL

Materials

Samples of PBT chip, xylene, 1,2-dichlorobenzene, dimethylformamide, and dibutyltin oxide were supplied by Aldrich. Chloroform and diethyl ether were supplied by Fisons Chemicals, and flash silica (60 Å) by ICN Absorben. All of the reagents were used as received.

Extraction of cyclic oligomers from PBT chip

PBT chip ($M_v \simeq 38\,000$, 200 g) was extracted with mixed xylene isomers (500 ml) at a refluxing temperature

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of 140°C for 96 h under nitrogen. The xylene was removed on a rotary evaporator, leaving cyclic oligomers at a yield of 1 wt%.

Solution ring-chain reactions for PBT

PBT chip was dissolved in 1,2-dichlorobenzene at 180°C. The solution was refluxed in the presence of dibutyltin oxide (1.0 wt% with respect to the polymer) for 72 h at dilution ratios of 1/10, 1/30, 1/50, and 1/70 (polymer/solvent, weight/volume dilution ratio). At the end of the reaction time, the solution was cooled to room temperature at which point the polymer re-precipitated. The polymer was then filtered off and the cyclic oligomers isolated from 1,2-dichlorobenzene, by removal of the solvent on a rotary evaporator. Further drying of the oligomers was carried out under high vacuum (0.1 mmHg).

Column chromatography

The cyclic dimer of PBT was isolated using column chromatography, from a sample of cyclic oligomers obtained by a solution ring-chain reaction. The mixed cyclic oligomer sample was separated into individual cyclic oligomers of PBT $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$, (where $x = 2$–5, cyclic dimer to cyclic pentamer, monitored by t.l.c.), over flash silica (60 Å) gel using chloroform/diethyl ether (9/1 v/v) as the eluent. The cyclic dimer was obtained in a yield of 2 wt%, and it was recrystallized first from chloroform and then from dimethylformamide.

Gel permeation chromatography

The cyclic oligomers were analysed using a Knauer gel permeation chromatography (g.p.c.) instrument. This was equipped with four PL-gel 3 μm mixed-E columns supplied by Polymer Laboratories Ltd. The instrument was fitted with a Shimadzu RID-6A refractive index detector. Samples were analysed in chloroform solution at room temperature at a flow rate of 0.3 ml min^{-1}. The relative peak areas of each cyclic oligomer were estimated using Polymer Laboratories logical software.

Fast atom bombardment mass spectrometry

Fast atom bombardment mass spectra (f.a.b.m.s.) of the cyclic oligomers were obtained using an autospec f.a.b.m.s. with caesium ions as the bombarding particles and 3-nitrobenzyl alcohol as the matrix.

Liquid chromatography tandem mass spectrometry

The cyclic oligomers were analysed using h.p.l.c., using a Spherisorb S3 ODS2 column with a two solvent eluent: water (0.1% acetic acid) and acetonitrile (0.1% acetic acid) at a flow rate of 0.9 ml min^{-1}. The instrument was fitted with an ultraviolet detector functioning at a wavelength of 240 nm.

Further analysis was achieved using a Finnigan MAT TSQ 7000 triple quadrupole mass spectrometer. Atmospheric pressure chemical ionization (a.p.c.i.) in the presence of traces of ammonium ions were used. Further fragmentation was achieved using 30 eV argon in a collision cell.

Nuclear magnetic resonance spectroscopy

Proton nuclear magnetic resonance (^{1}H n.m.r.) spectra were obtained on a JOEL 270 MHZ spectrometer, using deuterated chloroform as the solvent.

X-ray crystallography

Data collection. The crystal of the cyclic dimer of PBT was mounted on a thin glass fibre with a coat of epoxy cement. X-ray data were collected on an Rigaku AFC6S diffractometer. Cell constants and an orientation matrix for the data collection were obtained from the least squares refinement of 20 automatically centred reflections. Equivalent reflections were merged and the data were corrected for Lorentz and polarization factors.

Structure solution. The crystal structure was solved by Direct methods using SHELXS86[21] and expanded using Fourier techniques with Direct Difference. This was then followed by full matrix least squares refinement on F^2 using SHELXL93. All non-hydrogen atoms were refined anisotropically and hydrogens were geometrically placed using a rigid model.

RESULTS AND DISCUSSION

Solution ring-chain reactions using 1,2-dichlorobenzene

The catalysts used in our previous investigation for solution ring-chain reactions of PET[1] were initially used for solution ring-chain reactions of PBT. These catalysts were tetraisopropyl orthotitanate, dibutyltin *bis*-(2-ethylhexanoate) and zinc acetate. However, for solution ring-chain reactions of PBT, these catalysts were found to be unsuccessful in producing substantial amounts of cyclic oligomers. Varying the dilution ratio (polymer/solvent, weight/volume) and the reaction time appeared to have no significant effect in increasing the yield of the cyclic oligomers of PBT formed in solution ring-chain reactions.

However, a series of solution ring-chain reactions performed using dibutyltin oxide catalyst (used in macrocyclic oligomer polymerizations[15]), proved most successful in the formation of cyclic oligomers of PBT. Increasing the dilution ratio substantially increased the yield of cyclic oligomers formed in the reactions. At a dilution ratio of 1/10, the yield of cyclic oligomers was 13 wt%, at a ratio of 1/30 it was 42 wt%, at 1/50 it was 56 wt%, and at 1/70 it was 70 wt%.

The g.p.c. trace for the cyclic oligomers extracted from chip together with the g.p.c. trace for the cyclic oligomers of PBT from a solution ring chain reaction are shown in *Figures 1a* and *1b* respectively. The g.p.c. traces show very similar product distributions, $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$, peaks are assigned to cyclics with $x = 2$–8. The percentage amounts of each cyclic oligomer were estimated by g.p.c. using Polymer Laboratories Logical software, and are listed in *Table 1*. The cyclic oligomers from these solution ring-chain reactions at different ratios gave similar product distributions with comparable amounts of each individual cyclic oligomer analysed by g.p.c.

H.l.p.c. traces of the extract of cyclic oligomers from chip as well as the cyclic oligomers from the solution ring-chain reaction are shown in *Figures 2b* and *2a* respectively. This shows cyclic oligomers $(CO.C_6H_4.CO.O.(CH_2)_4O)_x$, ranging from $x = 2$–9. The cyclic oligomers from the solution ring-chain reaction contained relatively larger amounts of the higher molar mass cyclic oligomers compared with the cyclic oligomers extracted from commercial PBT chip.

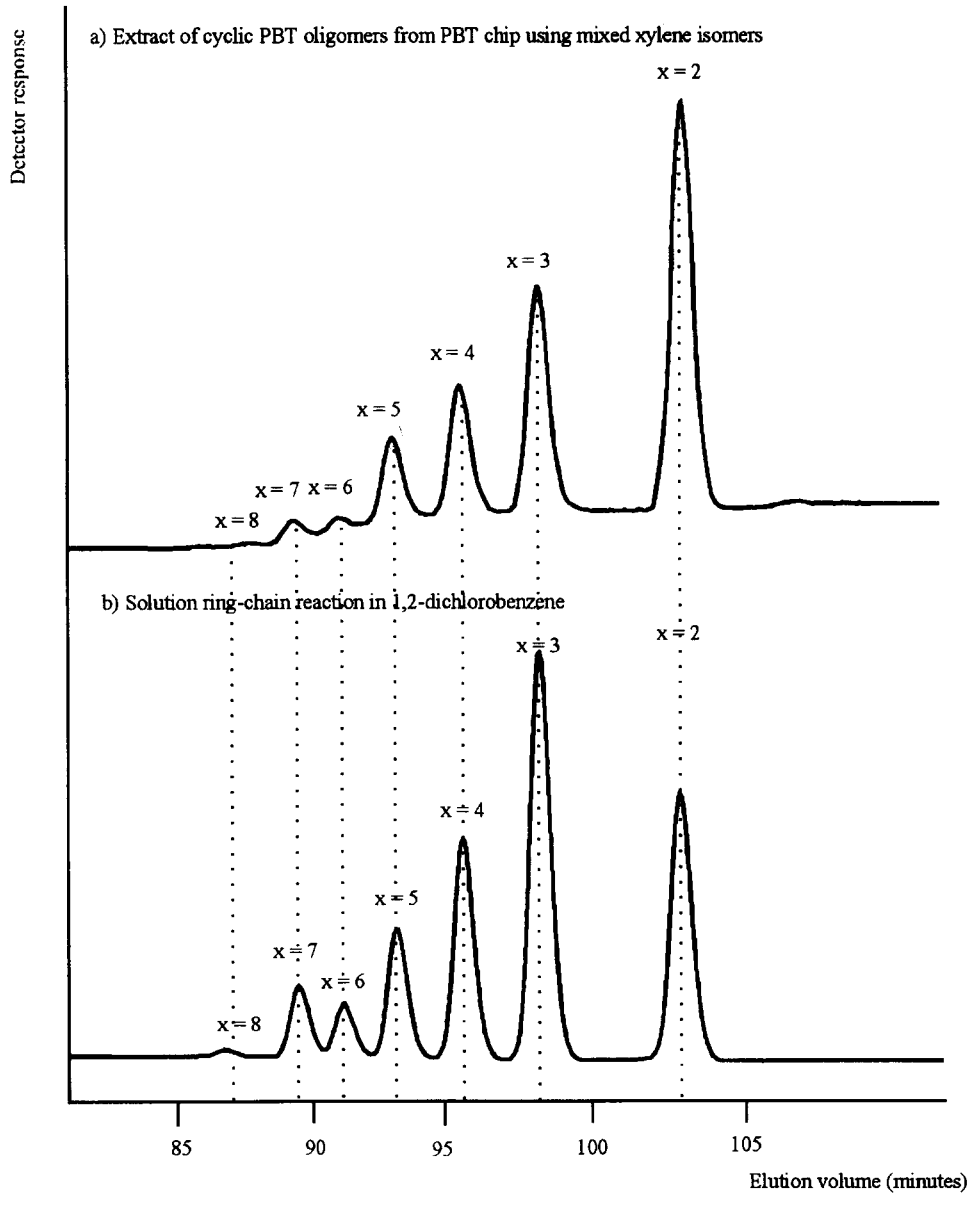


Figure 1 (a) G.p.c. of cyclic PBT oligomers extracted from chip with mixed xylene isomers. (b) G.p.c. of cyclic PBT oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene with dibutyltin oxide as catalyst

Table 1 Comparison of the percentage amounts of individual cyclic oligomers $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$ of PBT from an extract of commercial chip, with the percentage amounts of cyclic oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene (all estimated by g.p.c. as described in the text)

	% amount of individual cyclic oligomer of PBT	
Individual cyclic PBT oligomer (x)	Cyclic PBT oligomers extracted from chip (1 wt%)	Solution ring-chain reaction in 1,2-dichlorobenzene (1 : 10 dilution ratio, w/v, 13 wt%)
$x = 2$ (cyclic dimer)	49	25
$x = 3$ (cyclic trimer)	25	36
$x = 4$ (cyclic tetramer)	14	19
$x = 5$ (cyclic pentamer)	9	11
$x = 6$ (cyclic hexamer)	1	4
$x = 7$ (cyclic heptamer)	2	5
$x = 8$ (cyclic octamer)	<1	<1

^{1}H n.m.r. spectroscopy of the cyclic PBT oligomers showed three singlets: $\delta = 7.9$ ppm (aromatic), $\delta = 4.6$ ppm ($O.CH_2$ in the cyclic PBT ring unit) and $\delta = 2.0$ ppm ($CH_2.CH_2$ in the cyclic PBT ring unit), all characteristic of cyclic PBT.

Fast atom bombardment mass spectrometry

The cyclic oligomers of PBT both from the extract from commercial chip and the solution ring-chain reactions were analysed by f.a.b.m.s. A typical f.a.b.m.s. of cyclic oligomers of PBT from a solution

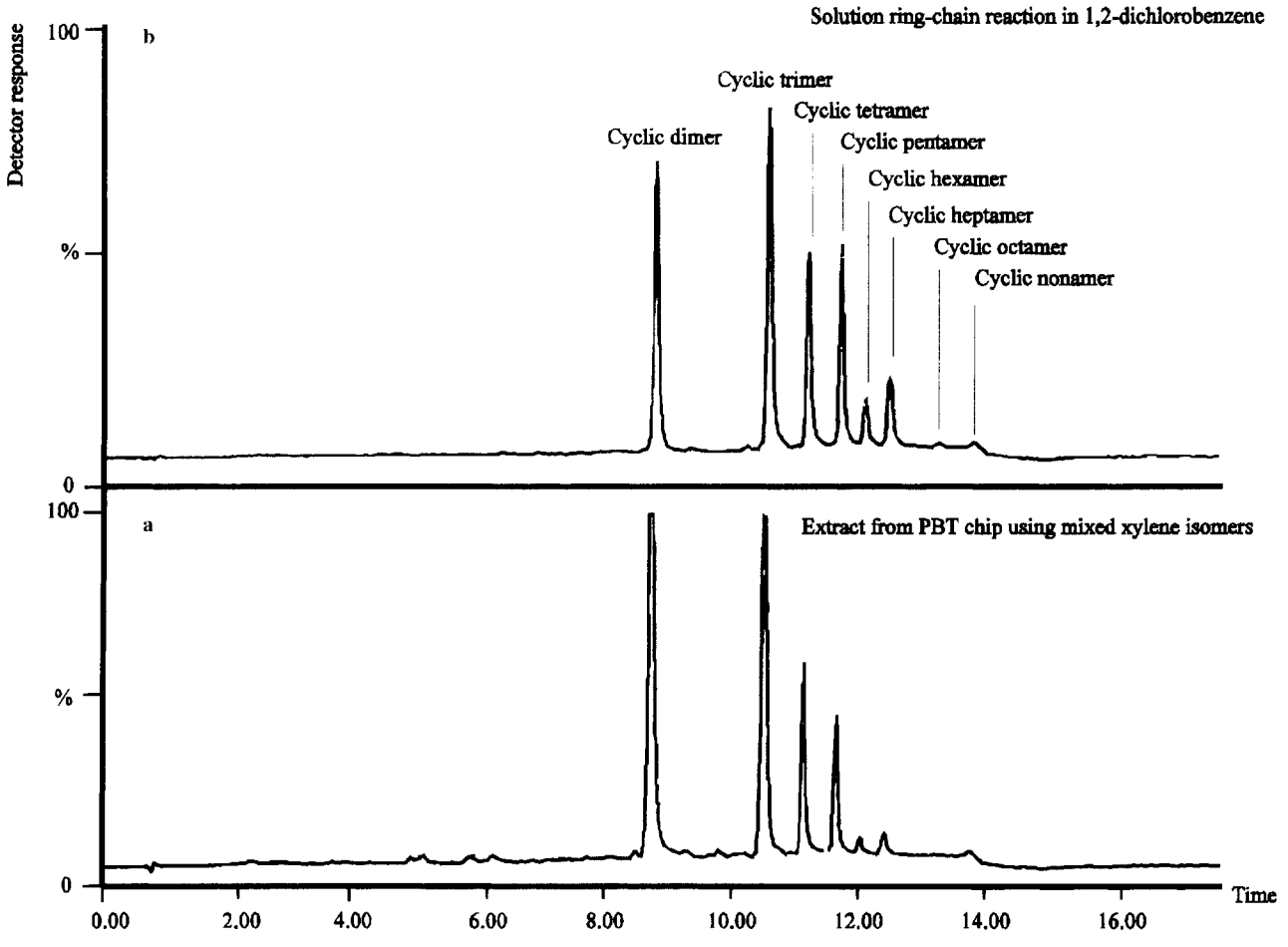


Figure 2 (a) H.p.l.c. trace of cyclic PBT oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene with dibutyltin oxide as catalyst. (b) H.p.l.c. trace of cyclic PBT oligomers extracted from chip with mixed xylene isomers.

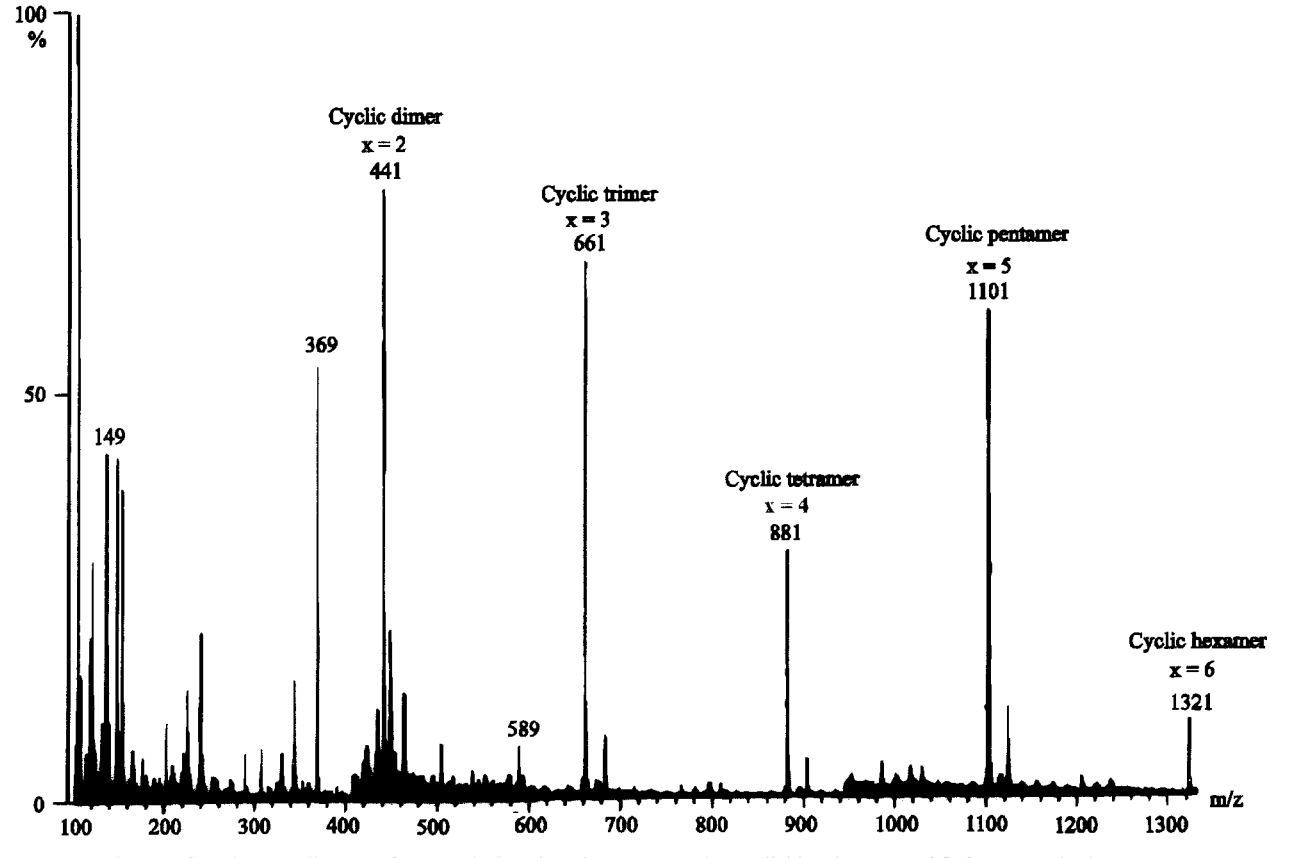
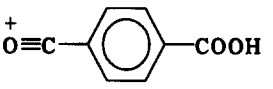
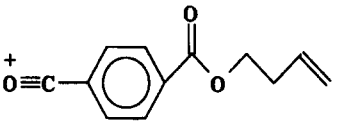
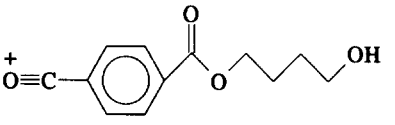
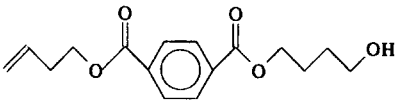
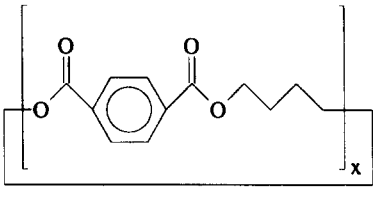


Figure 3 F.a.b.m.s. of cyclic PBT oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene, $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$, where $x = 2$–6

Table 2 Fragment structures and corresponding m/z values present in f.a.b.m.s. (of cyclic PBT, oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene) and the product-ion mass spectra of the cyclic trimer of PBT

Ion assignment	m/z	Ion structure
M^+	149	
M^+	203	
M^+	221	
Loss of ion structure (molecular weight 292) from cyclic trimer	369	
Loss of ion structure (molecular weight 72) from cyclic trimer	589	$CH_2{=}CH{-}CH_2{-}CH_2{-}OH$
M^+		
$x = 2$	441	
$x = 3$	661	
$x = 4$	881	
$x = 5$	1101	
$x = 6$	1321	

ring-chain reaction (shown in *Figure 3*) shows a regular series of spectral lines (M^+) corresponding to exact multiplets of the repeat unit $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$ (formula weight = 220.22) where $x = 2$–6. Furthermore, spectral lines are observed at $M^+ = 369$ and 589, these corresponding to the loss of the fragments shown in *Table 2* from the cyclic trimer of PBT.

Liquid chromatography tandem mass spectrometry

H.p.l.c. chromatograms of cyclic oligomers produced from the solution ring-chain reactions in 1,2-dichlorobenzene were characterized by the corresponding a.p.c.i. mass spectrum (shown in *Figure 4*).

Several ions were selected for liquid chromatography tandem mass spectrometry (l.c.-m.s.-m.s.) experimentation so that complementary structural information could be obtained. The positive ions selected were: m/z 463 $(M + Na)^+$, m/z 661 (M^+), m/z 881 (M^+), m/z 1101 (M^+), and m/z 1321 (M^+). The product-ion mass spectra are shown in *Figure 5*. The product-ion mass spectrum of the cyclic trimer of PBT (m/z 661 (M^+)) is also shown in *Figure 5*. This mass spectrum shows the fragmentation pattern of the cyclic trimer of PBT. The ion structure of the fragments from the cyclic trimer and their corresponding m/z values is shown in *Table 2*, these corresponding well with the detailed mass spectral work of cyclic oligomers of PBT by Montaudo *et al.*[7].

X-ray crystallography

The X-ray crystal structure of cyclic dimer of PBT has been published previously[9]. However, the purpose of the fractionation of the cyclic dimer of PBT and the subsequent crystallographic investigation was intended to demonstrate

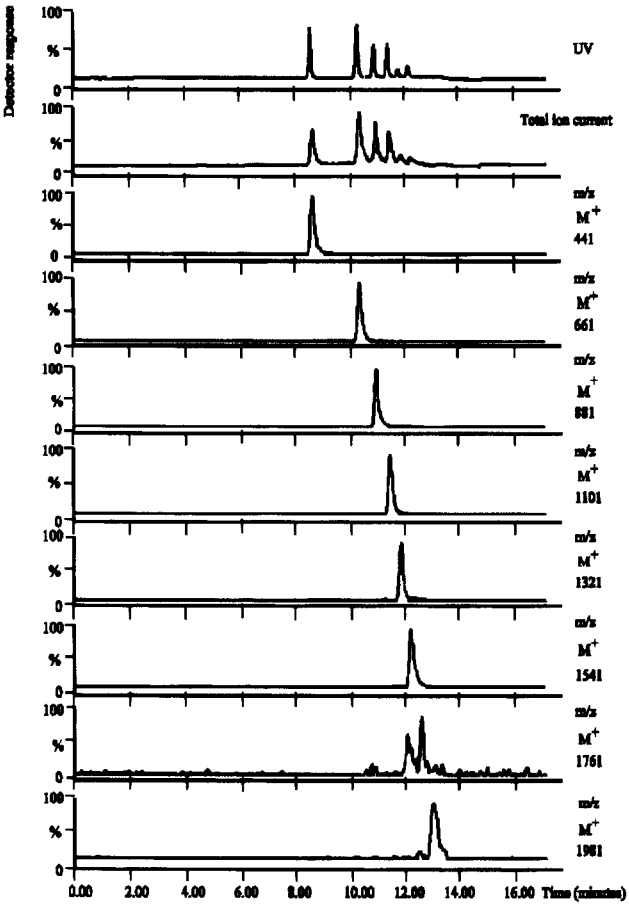


Figure 4 L.c.-m.s. for cyclic PBT oligomers from a solution ring-chain reaction in 1,2-dichlorobenzene, $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$, where $x = 2$–9. The corresponding m/z values were determined using a.p.c.i.m.s.

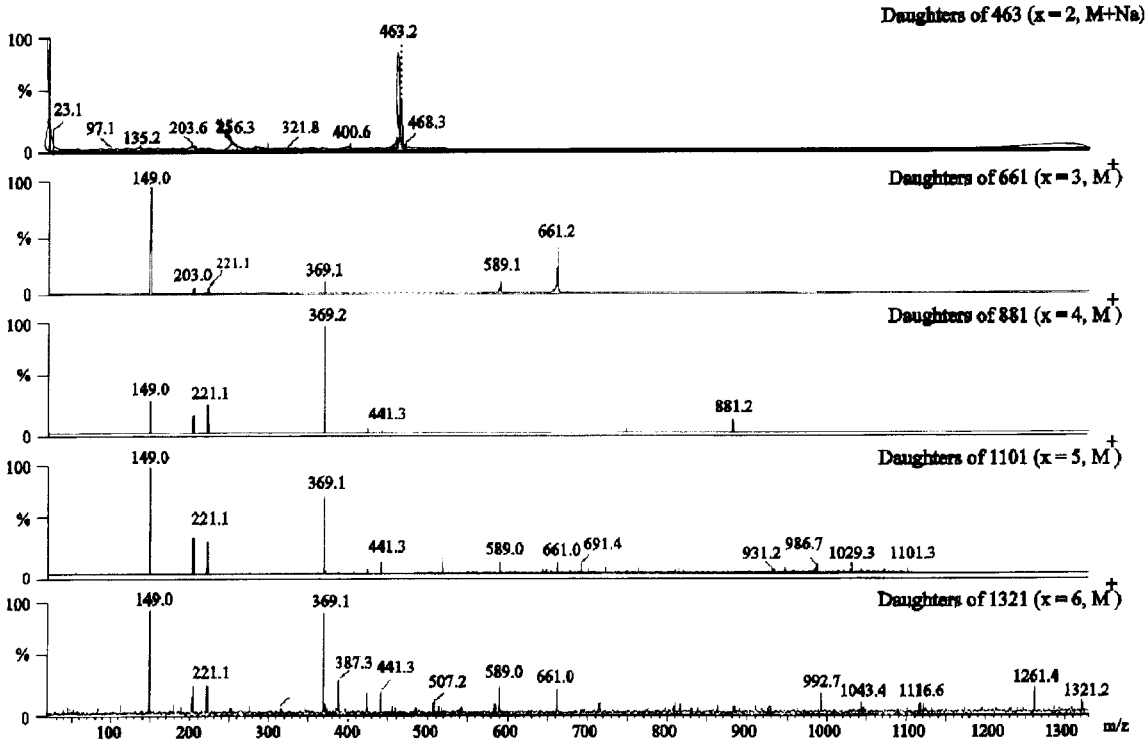


Figure 5 Product-ion mass spectra for the cyclic dimer, trimer, tetramer, pentamer, and hexamer of PBT $(CO.C_6H_4.CO.O.(CH_2)_4.O)_x$ where $x = 2$–6

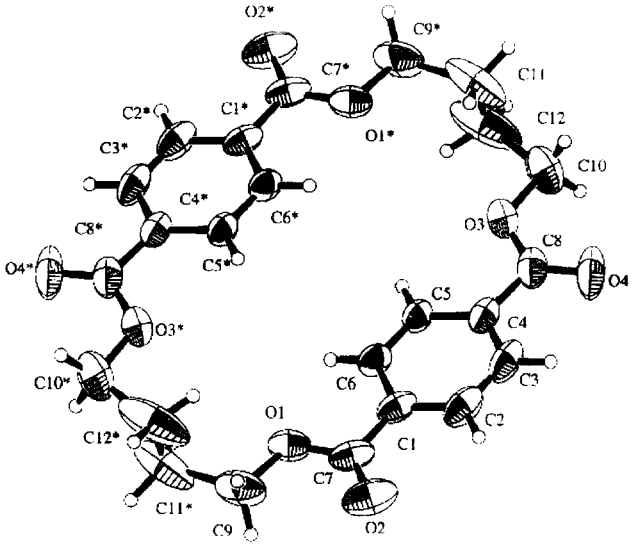


Figure 6 X-ray crystal structure of the cyclic dimer of PBT $(CO.C_6H_4.CO.O.(CH_2)_4.O)_2$

that the first cyclic oligomer eluted in the g.p.c. trace for the mixture produced by a solution ring-chain reaction in 1,2-dichlorobenzene is indeed the cyclic dimer (see *Figure 6*). The X-ray crystallographic study determined the *R* value as 0.087, which is in reasonable agreement to the published *R* value of 0.052 by Kitano *et al.*[9].

CONCLUSIONS

This investigation has shown how substantial quantities of cyclic oligomers can be prepared using solution ring-chain reactions in 1,2-dichlorobenzene using dibutyltin oxide as catalyst. These cyclic oligomers of PBT have been fully characterized. These macrocyclic oligomers have potential in commercial applications, and will be the subject of future investigations in our laboratory.

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