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Preparation and characterization of large ether–ester rings

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Cyclic oligomers of tetraethyleneglycol succinate $[O(CH_2CH_2O)_4.CO.(CH_2)_2.CO]_x$ were prepared by a ring–chain reaction. The cyclic products were characterized in full. Cyclic oligomers with up to eight repeat units were fractionated using preparative gel permeation chromatography to give narrow molar mass fractions with polydispersities of 1.03. The fraction consisting of the monomeric ring only was found to crystallize readily, enabling its X-ray crystal structure to be determined. © 1997 Elsevier Science Ltd.

(Keywords: large cyclic ether–esters; gel permeation chromatography; X-ray crystal structure)

Introduction

As part of a general study of cyclic oligomers and polymers[1–3], we have been developing synthetic routes to large ring esters[4–10]. Recent publications have included the preparation and characterization of cyclics in poly(decamethylene adipate)[8], poly(decamethylene terephthalate)[9] and poly(ethylene terephthalate)[10] systems.

In this communication, we show how large cyclics can be prepared and characterized in an ether–ester system, poly(tetraethyleneglycol succinate) (PTGS). The preparation of the cyclic monomer and dimer have been prepared by alternative routes, but their crystal structures were not determined[11–13]. Here, it is shown that cyclics $[O(CH_2CH_2O)_4.CO.(CH_2)_2.CO]_x$ can be obtained in good yield by a ring–chain reaction. Using preparative gel permeation chromatography (g.p.c.) narrow molar mass fractions can be obtained containing cyclics with up to eight repeat units or 136 skeletal bonds. The cyclic monomer can be obtained as a pure compound, and its crystal structure has been determined. This new route to large cyclic ether–esters opens up the possibility of a whole range of new chemical compounds, some of which may form complexes with metal ions and act as conducting polymers[14].

Experimental

Materials. Tetraethylene glycol (97%) and dimethyl succinate (98 + %) were obtained from Lancaster Synthesis Co. The catalysts employed in the reactions, (dibutyltin bis(2-ethyl hexanoate)[15,16] and tetraisopropyl orthotitanate)[17–19] were obtained from Fluka Chemica. All of the above reagents were used as received with no further purification.

Preparation of PTGS. PTGS was prepared by a polymerization reaction between dimethyl succinate and tetraethylene glycol. The two reagents were added in equimolar proportions (0.35 mol) to a multi-necked round-bottomed flask equipped with an overhead stirrer, a nitrogen inlet, a thermometer and a distillation head. The contents of the flask were raised to a temperature of approximately 80°C with continuous stirring to ensure thorough mixing. The transesterification catalyst, tetraisopropyl orthotitanate (0.5 wt%) was added and the temperature raised to 120°C for a period of 18 h, during which time methanol was evolved and distilled off. The flask contents were then raised to 150°C for 24 h under vacuum (15 mmHg) to remove further methanol from the reaction in order to produce a mainly linear polymer.

Preparation of tetraethyleneglycol succinate rings. To favour the formation of poly(tetraethyleneglycol succinate) rings the chain polymer (15.0 g), prepared using the above procedure, was refluxed in chlorobenzene (800 ml, 130°C) under dilute solution conditions with dibutyltin bis(2-ethyl hexanoate) as the transesterification catalyst for 96 h. The progress of the reaction was monitored by removal of 5.0 ml samples at regular daily intervals. Each sample was rotary evaporated to dryness and then analysed by analytical gel permeation chromatography (g.p.c.). The total product after 96 h was collected and rotary evaporated to dryness and then analysed by g.p.c., and nuclear magnetic resonance (n.m.r.) and FAB mass spectroscopy.

G.p.c. The products from both polymerization and cyclization reactions were analysed using a g.p.c. instrument. The instrument used was a Knauer chromatograph equipped with four PLgel 3 μm mixed-E columns connected in series. The instrument was supplied by Polymer Laboratories and was fitted with a Shimadzu RID-6A refractive index detector. Samples were analysed in chloroform at ambient temperature at a flow rate of 0.3 ml min^{-1}. The instrument was calibrated using narrow molar mass polystyrene standards.

The tetraethyleneglycol succinate rings were fractionated on a preparative g.p.c. instrument to give a series of sharp molar mass fractions. The instrument used two

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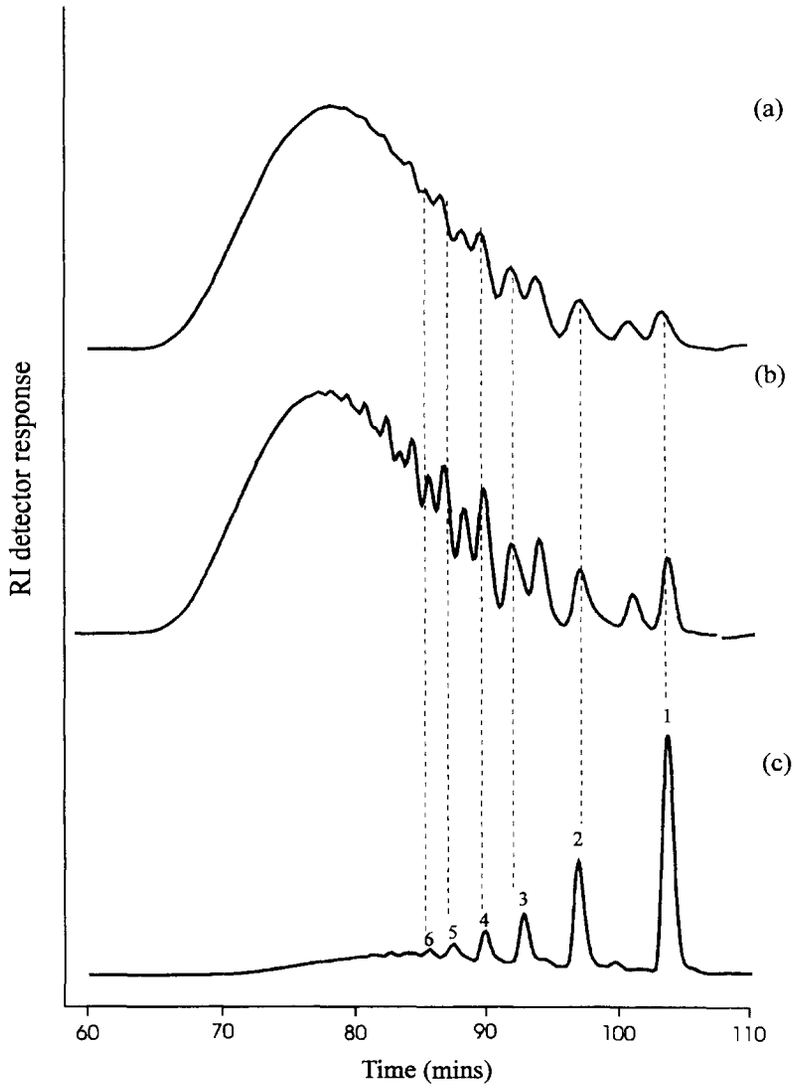

Figure 1 G.p.c. chromatograms for the tetraethyleneglycol succinate oligomers observed at time intervals of (a) 0, (b) 12 h and (c) 72 h. The number of repeat units of the oligomer are indicated

5 μm ultrastryragel columns connected in series and was supplied by Waters (Millipore) Ltd. Toluene was used as the eluent.

N.m.r. spectroscopy. ^{1}H n.m.r. spectra were obtained using a Joel 270 MHz spectrometer. The samples were dissolved and analysed in deuterated chloroform.

Mass spectroscopy. FAB mass spectra of the cyclic products were obtained using an Autosopec spectrometer, using dichloromethane as solvent.

Results and discussion

The melt polymerization of dimethyl succinate and tetraethylene glycol with the liberation of methanol produced a broad low molar mass linear polymer. This was a lower average molar mass than was achieved for the poly(decamethylene adipate) system (under similar temperature conditions) and may possibly be due to the different catalysts used. The g.p.c. analysis showed that the polymer had a weight average molar mass of 4000 with a polydispersity of 2.1 (*Figure 1a*).

The ring–chain transesterification reaction was carried out under dilute solution conditions with a solvent-to-polymer ratio of *ca.* 50/1 (w/w) and monitored by g.p.c. analysis at regular intervals. It was shown that after 12 h the concentration of low molar mass cyclics had started to increase (*Figure 1b*). After 72 h the higher molar mass chains had been transformed into cyclic oligomers and cyclics with up to six repeat units were clearly resolved (*Figure 1c*). From the g.p.c. tracings the yield of cyclic oligomers was found to be approximately 90 wt%.

The cyclic oligomers were fractionated by preparative g.p.c. to give a series of narrow molar mass samples with polydispersities of about 1.03 (*Figure 2*). The high resolution of the preparative columns enabled fractions containing only the monomeric and dimeric rings to be collected as individual compounds, with very little contamination from other low molar mass oligomers. The n.m.r. spectra of the fraction consisting of the monomeric ring showed the absence of end groups. Four sets of signal responses were observed as follows: a singlet at $\delta = 2.69$ ppm due to protons adjacent to the carbonyl group of the ester linkage (–CO–C$\underline{H}_2$C$\underline{H}_2$–CO.O–), a triplet at $\delta = 4.27$ ppm due to protons immediately adjacent to the oxygen of the ester linkage (–C$\underline{H}_2$–O.CO–), a strong singlet at

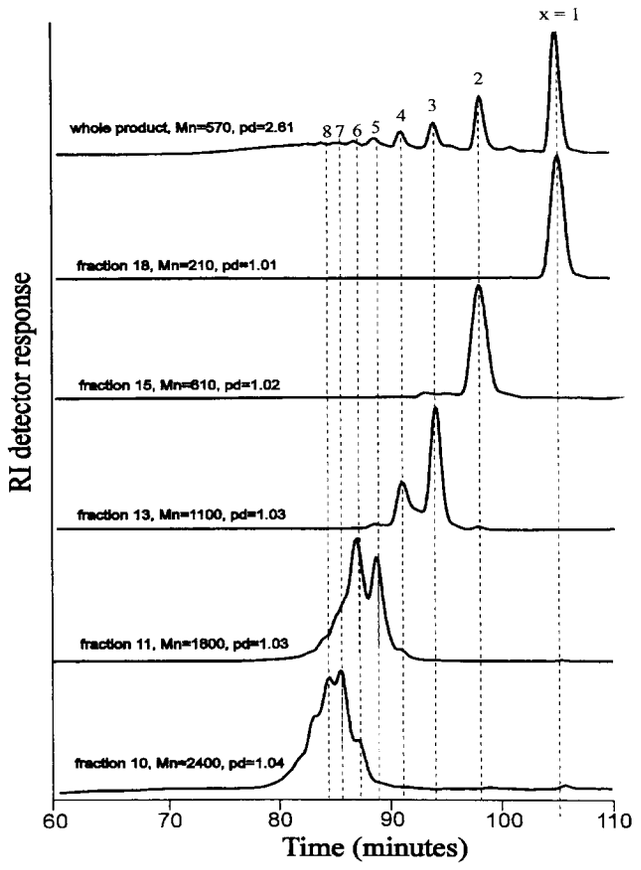

Figure 2 G.p.c. chromatograms of cyclic tetraethylene glycol succinate oligomers fractionated using preparative g.p.c. The number of observable repeat units for the cyclic oligomers are indicated ('pd' denotes polydispersity)

$\delta = 3.67$ ppm due to protons of the oxyethylene backbone $(-C\underline{H}_2C\underline{H}_2-O-)_n$ and a triplet at $\delta = 3.72$ ppm due to protons of the oxyethylene group adjacent to the ester groups $(-C\underline{H}_2C\underline{H}_2-O.CO-)$ with an integral ratio of 11:21, respectively. The n.m.r. spectra of higher molar mass fractions consisting of four, five, six and higher rings showed that some chain species were present, but only in small amounts. FAB mass spectra confirmed the presence of cyclic species consisting of up to six repeat units in the various fractions. Due to the limitations of the FAB mass spectrometric technique higher molar mass species could not be resolved.

The fractions containing the monomeric ring only were found to crystallize readily from the melt. Crystals suitable for X-ray diffraction were grown from dilute solution in pentane. The crystals were obtained as thin rectangular plates. The X-ray crystal structure was determined and it gave conclusive evidence for the cyclic nature of the monomer (*Figure 3*). The detailed results from this X-ray crystallographic determination will be published separately[20].

With the high resolution of the analytical g.p.c. columns it should be possible to separate and isolate individual ring species of up to six repeat units. This work is planned and will form part of future investigations.

Conclusions

This present study has demonstrated that large cyclic ether–esters from tetraethylene glycol and dimethyl succinate can be prepared with up to eight repeat units in good yield, and that evidence is given from n.m.r., g.p.c., mass spectroscopy and X-ray crystallography for their cyclic nature. The rings produced should

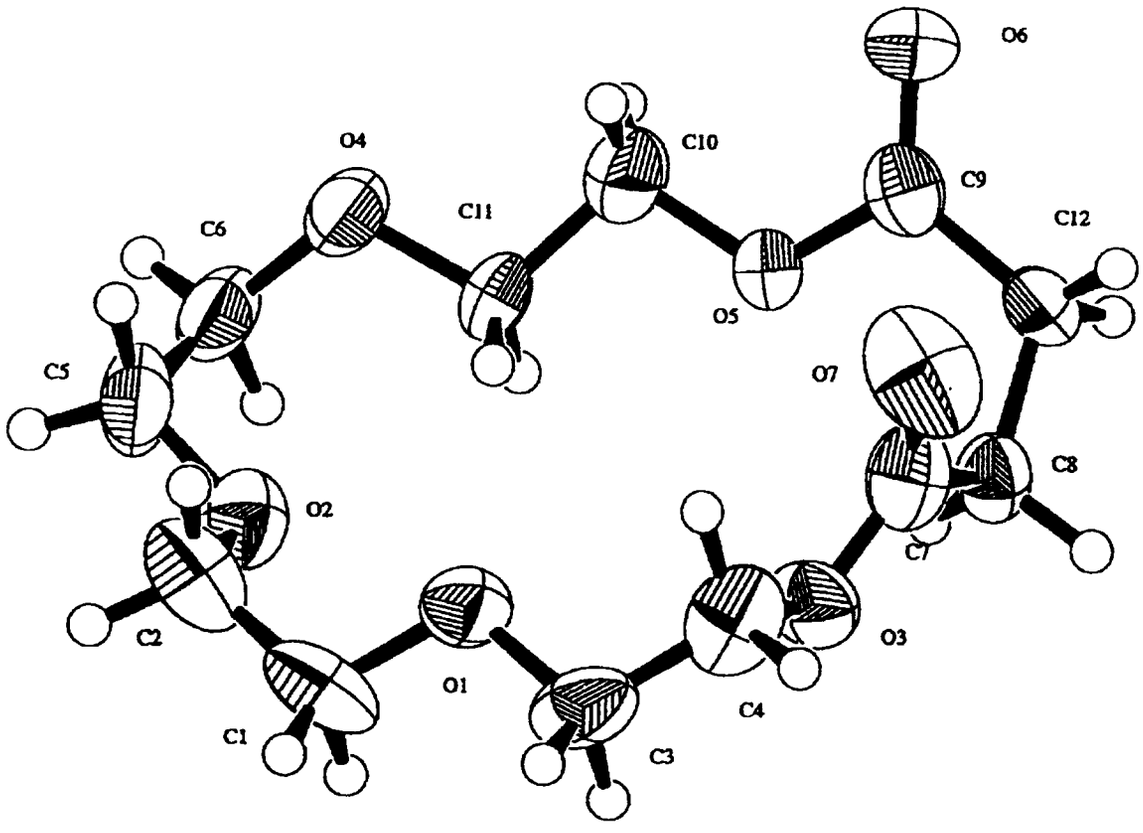

Figure 3 X-ray crystallographic representation of the structure of the tetraethyleneglycol succinate ring

demonstrate strong complexation or binding with metal ions or polar molecules in similar ways to that of crown-ethers, for example 18-crown-6. Such binding/complexation properties will be investigated as part of our future work.

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