Cyclic polyesters: 3. Attempts to prepare catenated polymers using polymer-supported reagents

B. R. Wood and J. A. Semlyen*
Chemistry Department, University of York, Heslington, York YO1 5DD, UK

and P. Hodge
Chemistry Department, University of Manchester, Oxford Road, Manchester M13 9PL, UK
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A range of reactions have been carried out using 11-bromoundecanoic acid attached to polymer supports in an attempt to prepare the first catenated polymers. In one series of reactions, cyclization of the polymer-supported polyester chains was effected in the presence of sharp fractions of polydimethylsiloxane rings, but no evidence of catenane formation could be found. Instead, a white crystalline product polyester was obtained. Its identity is discussed here. In another series of reactions, polymer-supported linear polyesters were cyclized in the presence of recycled cyclic polyesters. Gel permeation chromatographic analyses showed that substantial quantities of high molar mass material had been formed. This material may prove to be the first catenated polyesters to be prepared.

(Keywords: cyclic polyesters; catenated polymers; polymer supports)

INTRODUCTION

The science of linear polymers is well developed after nearly a century of endeavour by thousands of polymer scientists worldwide. By comparison, the science of cyclic polymers has received attention from only a few scientists and most of the advances that have been made during the past 30 years are reviewed in just two books[1,2]. Yet nature has demonstrated the power and versatility of the large ring as a unit of molecular structure in the biochemistry of cyclic DNA. For example, cyclic DNA can catenate, supercoil and form permanent knots—all beyond the capabilities of long chain molecules[3,4].

Recently, Stoddart *et al.*[5,6] have produced the first of what they term 'molecular train sets', where they suggest that a small ring (a 'train') travels rapidly around a large ring with 'stations' spaced at intervals around it. They believe that this system could prove to form the basis of high speed molecular computers of the future. In addition, Brunelle and Shannon[7] have prepared cyclic polycarbonates, which can be used to make higher molar mass linear polycarbonates than can be obtained any other way. Furthermore, Gibson *et al.*[8–10] have recently modified linear polymers by threading crown ethers on to their structures to give polyrotaxanes. All these advances suggest that the exploration of large ring molecules and cyclic polymers will result in new, useful materials for the next century.

Following our theoretical and experimental studies of cyclic concentrations in polymeric systems[11,12] and our preparation, characterization and investigation of the first synthetic cyclic polymers[13], we are now exploring the preparation of new cyclic polymers using polymer-supported reagents[14–17]. The application of polymer-supported reagents for the preparation of cyclic polymers is an idea first proposed by Hodge *et al.*[18].

In part 1 of this series[16], the first synthetic cyclic polymers prepared by the use of polymer-supported reagents were described. These were cyclic polyesters $[(CH_2)_{10}CO.O]_x$ and they were characterized by g.p.c., n.m.r. spectroscopy, fast atom bombardment (f.a.b.) mass spectroscopy and by trapping the rings into networks[17]. The polymer-supported reaction is believed to proceed by the mechanistic steps shown in *Figure 1*. The reaction can be described in two parts: neutralization of the bicarbonate form of the polymer support by 11-bromoundecanoic acid followed by chain growth and cyclization of the resulting supported polymers. Chain growth is believed to occur by an intermolecular alkylation reaction due to nucleophilic substitution of a bromine atom on an adjacent polymer-supported monomer or polymer unit. The resulting bromine terminated carboxylate chain remains ionically bound to the polymer support. Cyclization is believed to result by an intramolecular alkylation reaction as a consequence of nucleophilic substitution of a bromine atom by the carboxylate anion of the same molecule. The resulting neutral ring is consequently released from the polymer support.

In principle, the polymer-supported reaction can be used to synthesize the first polymeric catenanes and attempts to prepare such catenanes are described in this paper. An outline of the approach is illustrated in

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* To whom correspondence should be addressed

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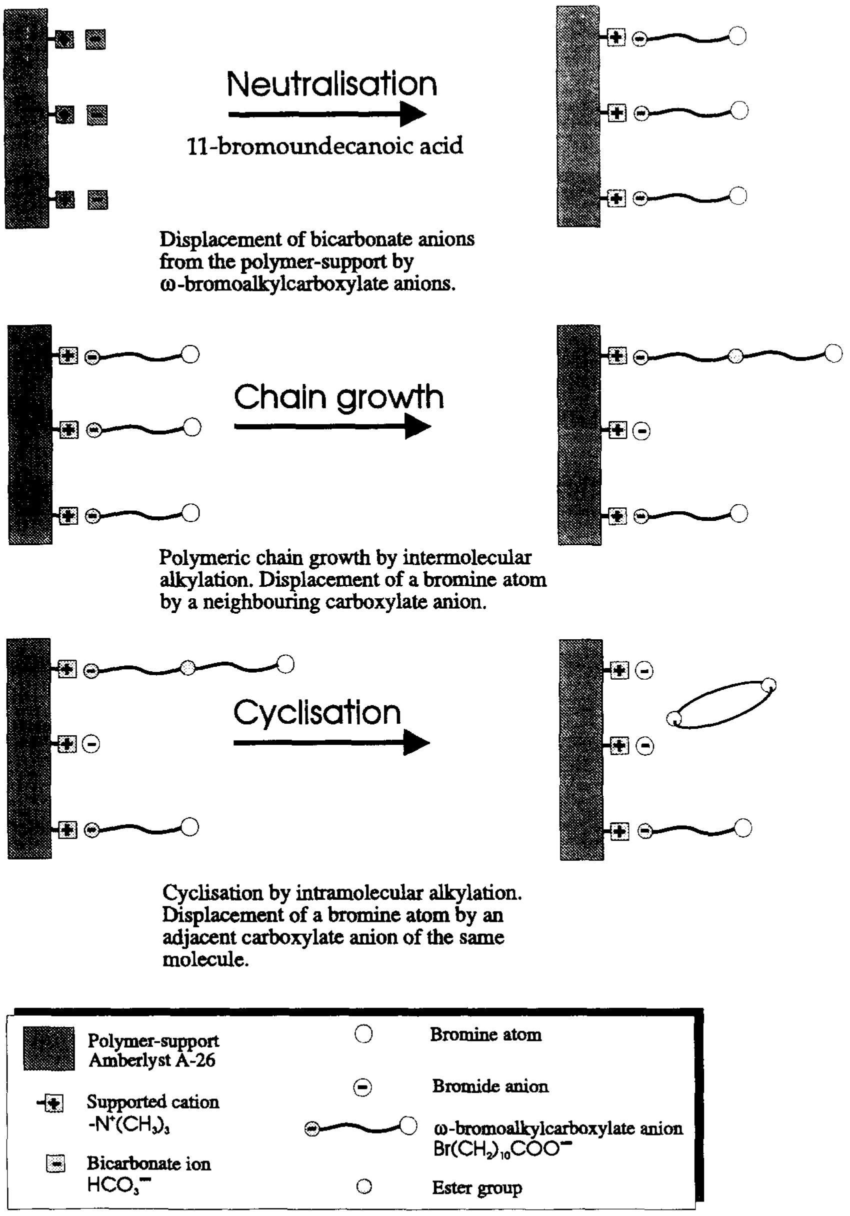


Figure 1 The polymer-supported reaction

Figure 2. This shows how catenanes may be formed when intramolecular cyclization reactions are carried out in the presence of cyclic polymers. This novel approach has been applied here using cyclic polyesters produced by polymer-supported reactions and using cyclic polydimethylsiloxanes (PDMS) prepared previously[13], both without stirring. With cyclic polyesters, g.p.c. analysis indicated that polymeric material thought to be the first polymeric catenanes had indeed been formed in good yield. By contrast, with cyclic PDMS no polymeric catenanes appeared to have been formed, instead a white crystalline material was obtained and its identity is discussed in this paper.

EXPERIMENTAL

Materials

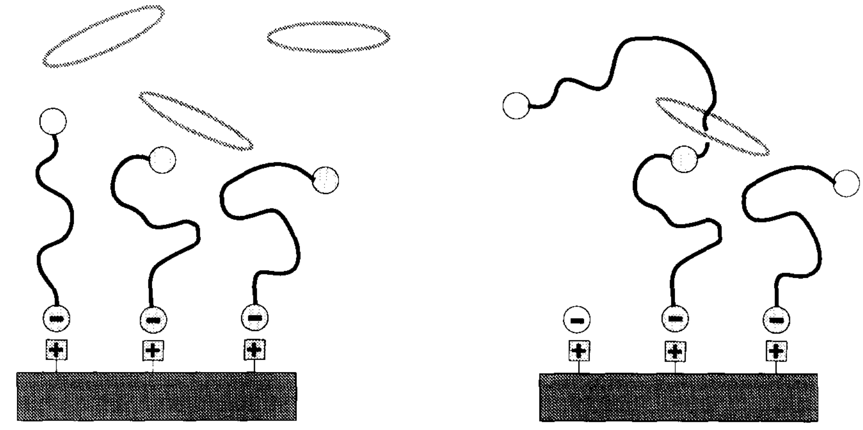
The polymer support used in this investigation was an anion exchange resin, Amberlyst A-26, supplied by Janssen Chimica. The resin, supplied in the chloride form, $P\text{-}N^+(CH_3)_3\ Cl^-$ was converted to the bicarbonate form $P\text{-}N^+(CH_3)_3\ HCO_3^-$ by ion-exchange using an aqueous saturated potassium hydrogen carbonate solution[16]. The concentration of bicarbonate ions residing on the resin was determined by pH back titration and was typically found to be 2–3 mmol g^{-1}.

The monomer used in the investigation was 11-bromoundecanoic acid [$Br(CH)_{10}CO_2H$], also supplied by Janssen Chimica.

Fractions of cyclic PDMS with heterogeneity indices M_w/M_n of ≈ 1.05 (where M_n represents the number-average molar mass and M_w represents the weight-average molar mass) had been prepared previously and were used in some of the reactions.

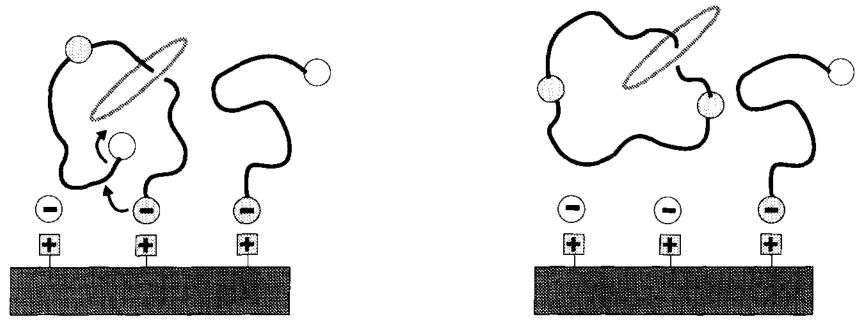
Resin preparation

The monomer loaded resin was prepared by neutralizing the bicarbonate form of the polymer support with a 11-bromoundecanoic acid solution. The anion-exchange resin in the bicarbonate form (≈ 80 g) was neutralized by a



(I) Polymer - supported monomer in the presence of a cyclic polymer.

(II) Statistical threading of a polymer ring by a growing polymer chain (via an intermolecular alkylation reaction).



(III) Ring closure polymerisation via an intramolecular alkylation reaction.

(IV) Polymeric catenane formation.

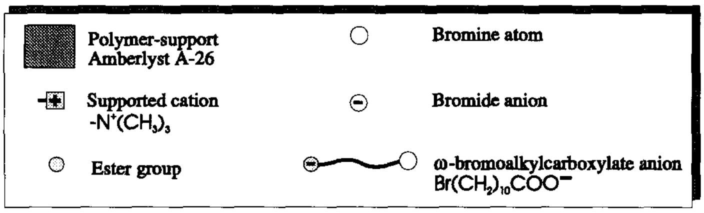


Figure 2 Reactions that could result in the formation of polymeric catenanes

methanolic 11-bromoundecanoic acid solution (0.14 mol, 38.2 g in ≈300 ml of methanol). The mixture was rapidly stirred in a round-bottom flask at room temperature for 24 h. The resin was collected by vacuum filtration, washed with methanol, deionized water and finally acetone and partially dried on a Buchner funnel by drawing air through it. The resin was further dried in a vacuum oven (≈2 mm Hg) at room temperature for ≈48 h. The uptake of the monomer unit was then determined by weight. Whilst not in use, the dried monomer-loaded resin was maintained at ≈5°C in a refrigerator.

Chain growth and polymerization

The chain growth and cyclization steps of the polymer-supported reaction of 11-bromoundecanoic acid were carried out employing four different procedures. The first procedure, reaction **A**, was described in part 1 of the series[16] and involves continuous stirring. The second, reaction **B**, and subsequent procedures, reactions **C** and **D**, were carried out on a smaller scale with the aim of preparing polymeric catenanes (see *Figure 2*).

A. Preparation of a mixture of simple cyclic polymers with stirring. The dried polymer-supported monomer (≈120 g, 30 wt% monomer) was placed in a two-necked round-bottom flask with ≈400 ml of toluene. The temperature was raised to 65°C and maintained at this temperature. The mixture was stirred continuously (≈280 rev min^{-1}) for the duration of the reaction (168 h). The resin was collected by vacuum filtration and washed twice with toluene. The product solution and washings were combined and then evaporated to dryness in a preweighed flask on a rotary evaporator.

B. Preparation of a mixture of simple cyclic polymers without stirring. Approximately 3.0 g of the monomer loaded resin (24 wt% monomer) and 5 ml of toluene were placed in a stoppered test tube and shaken by hand for ≈1 min. The test tube was sealed around the top with PVC tape and enclosed in a polyethylene bag to prevent ingress of water. The test tube was then suspended in a water bath at 65°C for 24 h. The product solution was decanted and the resin transferred to a 250 ml round-bottom flask and washed with toluene (≈ 100 ml). The resin was rapidly stirred for 4 h after which time the toluene was decanted. The resin was then washed a total of three times. The product solution plus the washings were combined and evaporated to dryness in a pre-weighed flask on a rotary evaporator.

C. Preparation of a mixture of simple cyclic polymers in the presence of large cyclic siloxanes without stirring. (i) Without recycling. In an attempt to prepare polymeric catenanes the above test tube scale experiments were carried out as for the preparation of B using the same quantities of reactant and solvent in the presence of PDMS rings (previously prepared at York). The procedure was carried out using 0.3 g quantities of PDMS rings (with a number-average number of skeletal bonds $n_n = 55$, 79 or 114 bonds). In addition a control experiment was carried out using PDMS chains of 134 bonds.

(ii) Recycling. In order to give every possible chance for the PDMS rings to be threaded by polymer-supported growing chains, the reaction products were recycled, i.e. further reacted with fresh monomer loaded resin. Test tube scale reactions were set up with ≈ 3.0 g of the monomer loaded resin, and this time 0.1 g of PDMS rings ($n_n = 55$, 79 or 114 bonds) and 5 ml of toluene. The test tubes were sealed and placed in a water bath at 65°C for 24 h. The product solution was decanted and the resin washed with toluene three times. The product solution and washings were combined and the solvent removed using a rotary evaporator. The reaction product was redissolved in 5 ml of toluene, placed in a test tube with a further 3.0 g of the monomer loaded resin, sealed and placed in the water bath for a further 24 h at 65°C.

D. Preparation of cyclic products involving the recycling of cyclic polyesters. A similar recycling approach to method C(ii) was carried out in an attempt to prepare catenated polyesters. In this case, no PDMS rings were added and the cyclic polyester products were recycled twice.

Gel permeation chromatography

The polyester products were analysed using an analytical gel permeation chromatograph. The instrument used was a Knauer HPLC/GPC equipped with a PL-gel 5 μm mixed-C size exclusion column and a guard column (both supplied by Polymer Laboratories Ltd). A Shimadzu RID-6A differential refractometer was used as the detector. HPLC grade toluene was used as the eluent at a flow rate of 1.0 ml min^{-1}. The instrument was calibrated using cyclic PDMS narrow molar mass samples ($M_w/M_n < 1.05$) (previously prepared at York)[1,2], in this connection it is noted that the characteristic ratio of liner PDMS (6.2 at 70°C)[19] is close to that of the linear polyester (which has been calculated to be 6.8 at 25°C)[17]. Two PL-gel 5 μm mixed-E columns were also used with AR-grade tetrahydrofuran as the solvent.

Melting point measurements

The melting point range of the polyester products was determined using a Gallenkamp melting point apparatus. An initial crude melting point range was determined using a heating rate of 5°C min^{-1}. A more accurate melting point range was determined using a heating rate of 2°C min^{-1}. The melting point determination was repeated twice for each sample and the average range recorded.

Spectroscopic methods

The ^{1}H n.m.r. spectra of the polyester products were obtained using a 90 MHz n.m.r. spectrometer and a 500 MHz n.m.r. spectrometer with deuterated chloroform as the solvent.

The mass spectra of the polyester products were obtained using an Autospec f.a.b. mass spectrometer.

Trapping of rings in networks

In order to verify the cyclic nature of polymeric products from reaction A, experiments were carried out to discover whether they could be trapped in PDMS networks[20–28]. The polymer networks were prepared by the crosslinking reaction between hydroxyl terminated PDMS chains ($M_n \approx 18\,000$) and tetraethylorthosilicate (TEOS). The reactions were catalysed by tin (II) ethylhexanoate with toluene as the solvent. The network trapping experiments were performed in duplicate.

The following procedure was used. The PDMS chains (4.0 g), TEOS (0.025 g) and the polyester product (≈ 0.08 g) were dissolved in toluene (4.0 ml). The solution was allowed to stand for 12 h and then mechanically shaken for 4 h. The catalyst (0.04 g) was added and the mixture further shaken for 20 min after which time the viscosity noticeably increased. After a standing time of 2 min, to allow air bubbles to disperse, the solutions were poured into PTFE moulds (60 mm x 60 mm x 3 mm). The networks were left to stand for 5 days at room temperature and pressure and then placed in a vacuum oven at 55°C (≈ 2 mm Hg) for 7 days. In addition, a control network was prepared, with no polyester product, to determine the network sol fraction.

The untrapped polyester product and non-network residues were extracted from the networks by swelling in methanol/toluene mixtures. Each network was carefully removed from its mould, divided in two, weighed and placed in screw-top bottles with mixtures of methanol/toluene (25–100% toluene) for a period of 7 days. The swollen networks were dried in a vacuum oven (55°C, ≈ 2 mm Hg) for 48 h and then weighed. The percentage of trapped product was calculated using the network weight loss (allowing for the weight loss due to the network sol fraction).

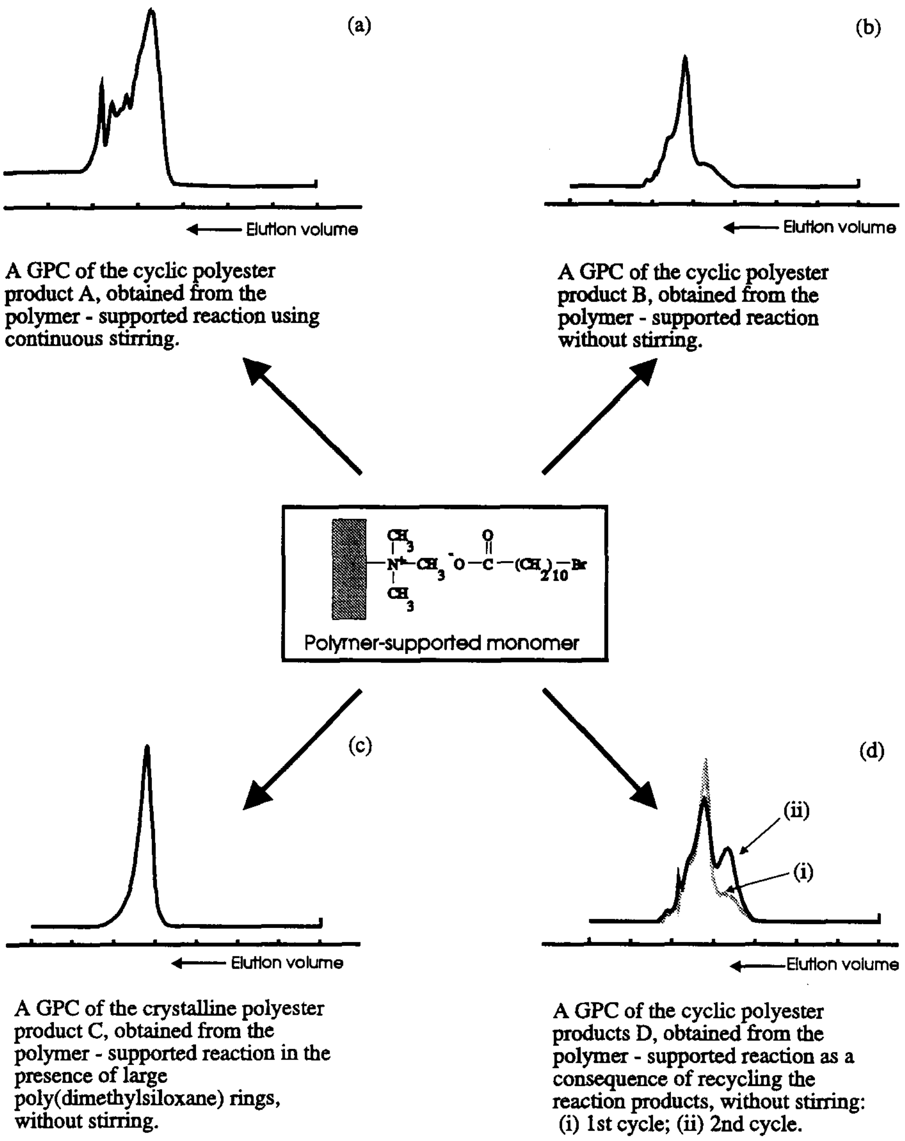
RESULTS AND DISCUSSION

Characterization of the products from the reactions

Reaction A. This reaction was carried out several times using the method described in the Experimental section, with stirring throughout. The products were analysed by g.p.c. and a typical trace is shown in *Figure 3a*. N.m.r. spectroscopy, f.a.b. mass spectroscopy and network trapping experiments established the products as mixtures of cyclic polyesters $[(CH_2)_{10}CO.O]_x$ as described previously[16,17]. Typical yields of cyclic products were ≈ 50 wt%.

Reaction B. The method described as method A in the Experimental section was adapted on a test tube scale with no stirring as outlined in the Experimental section. G.p.c. analysis showed quite a different distribution of products from those obtained by reaction A, with a much narrower distribution of cyclic polyesters (as shown in *Figure 3b*).

Reaction C(i). This reaction was carried out as described in the Experimental section. The reaction only



A GPC of the cyclic polyester product A, obtained from the polymer - supported reaction using continuous stirring.

A GPC of the cyclic polyester product B, obtained from the polymer - supported reaction without stirring.

A GPC of the crystalline polyester product C, obtained from the polymer - supported reaction in the presence of large poly(dimethylsiloxane) rings, without stirring.

A GPC of the cyclic polyester products D, obtained from the polymer - supported reaction as a consequence of recycling the reaction products, without stirring: (i) 1st cycle; (ii) 2nd cycle.

Figure 3 G.p.c. traces of products obtained from different polymer-supported reactions

differed from that of reaction B in that 0.3 g of PDMS rings were added. Three reactions were performed using cyclic PDMS fractions with $n_n = 55$, 91 and 114, respectively, and with heterogeneity indices $M_w/M_n \approx 1.05$. All three experiments were later repeated to ensure the consistency of the results. The cyclic PDMS fractions were added in an attempt to prepare catenated polyester/PDMS. No evidence for such catenated products was found and the g.p.c. trace was dominated entirely by the PDMS peak. N.m.r. spectroscopy of the dried product was in agreement with that expected for a mixture of a polyester and cyclic PDMS $[(CH_3)_2SiO]_x$. The dried product was redissolved in Analar toluene ($\approx 10\%$ w/w) and left to stand at room temperature for ≈ 7 days. A white crystalline material was observed to have formed in substantial amounts. This product melted over a narrow range (80.8–81.5°C). G.p.c. analysis of the crystalline material using a PL-gel 5 μm mixed-C column is shown in *Figure 3c*. Analysis using two PL-gel 3 μm mixed-E columns resolved the product into a number of components with a M_n of ≈ 2000.

The 90 MHz n.m.r. spectrum of the crystalline product (*Figure 4*) was that expected of linear or cyclic polyester(s). There was a single, small, sharp peak located at $\delta \approx 3.75$ ppm which could correspond to a methyl terminated ester. The 500 MHz n.m.r. spectrum (*Figure 5*) suggested that small quantities of end-groups were present (for example, the bands at $\delta \approx 3.38$ and 3.62 ppm may correspond to $-CH_2-Br$ and $-CH_2-Cl$, respectively).

The f.a.b. mass spectrum of the crystalline product was dominated by spectral lines corresponding to the cyclic polyesters $[(CH_2)_{10}CO.O]_x$ in decreasing intensity from $x = 2$ to 9 (*Figure 6*). This spectrum taken together with g.p.c. evidence suggests that rearrangement of the polyesters might have taken place in the mass spectrometer. Such rearrangements are not uncommon and are in accord with the known chemistry of esters and polyesters.

All these characterization methods suggest that relatively high molar mass polyesters have been produced on a substantial scale. The product solution from the control experiment, where PDMS chains with $n_n \approx 134$ replaced the cyclic PDMS, also gave a white crystalline product upon standing for ≈ 7 days. This indicates that the process governing the crystallization is not due to the cyclic character of the siloxane rings but rather to a

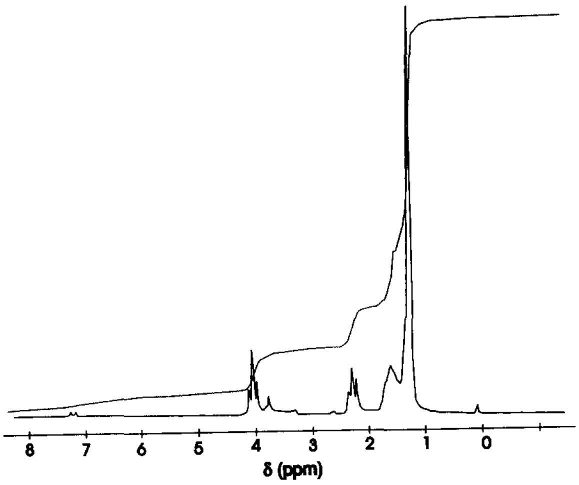


Figure 4 90 MHz n.m.r. spectrum of the crystalline product from reaction C(i)

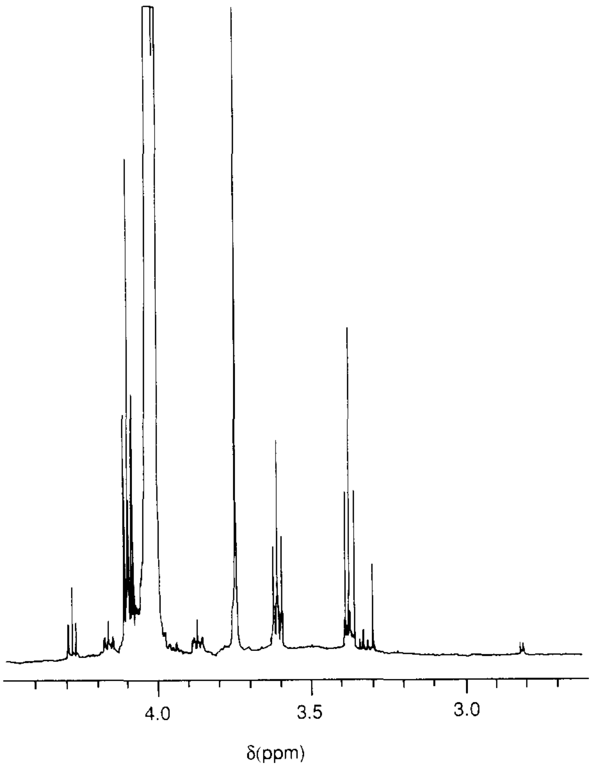


Figure 5 Part of the 500 MHz n.m.r. spectrum of the crystalline product from reaction C(i)

solution effect. Further preparations and investigations of this new material are in progress, for there is the possibility that if large cyclic esters are formed, they may adopt conformations in the crystalline state that are comparable to those of crown ethers[29] and furthermore that they may also form a range of complexes[30].

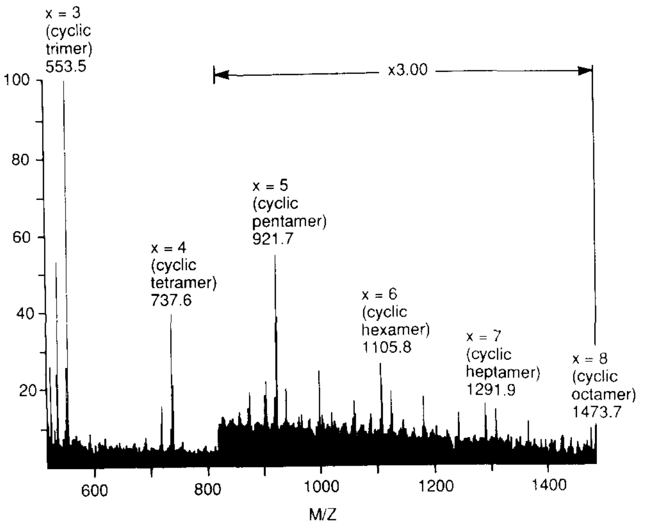


Figure 6 Part of the f.a.b. mass spectrum of the crystalline product from reaction C(i)

Reaction C(ii). The method C(i) described in the Experimental section was modified by recycling of the dried product of the reaction [method C(ii)] in further attempts to obtain a catenated polyester/PDMS product. G.p.c. analysis demonstrated that no such catenated product was formed. A white crystalline material was obtained, however, when the solution was left to stand. Examination of this showed that it was identical to the crystalline product obtained from reaction C(i).

Reaction D. The procedure described in the Experimental section for reaction D involved the recycling of the polyester rings in the absence of cyclic PDMS. Here g.p.c. analysis demonstrated that relatively high molar mass material with $n_n > 100$ was formed in good yield (*Figure 3d*). The n.m.r. spectrum of the total product corresponded to that of cyclic polyesters $[(CH_2)_{10}CO.O]_x$. The most likely explanation of the results is that the first catenated polyesters have been formed; such catenation would be expected to be probable because the rings involved are relatively large. They may be present in a mixture of dimeric, trimeric and higher order species. At present there are no techniques that could unequivocally establish their identity and there is always the possibility that simple ring molecules or even chain molecules have also been produced in the reaction. We plan to scale up the reaction and obtain sharp fractions by solution fractionation or preparative g.p.c.[31]. This would make it possible to perform network trapping and other experiments to assist in the characterization of the material.

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