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Cyclic polyesters: 4. Cyclics prepared by poly(decamethylene adipate) ring-chain reactions

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Ring-chain equilibration reactions of poly(decamethylene adipate) (PDA) were carried out in the presence of large amounts of diluent. Good yields of cyclics $[CO(CH_2)_4COO(CH_2)_{10}O]_x$ were obtained virtually free of linear species. The individual cyclics with 18–198 skeletal bonds were completely resolved using PL-gel mixed-E gel permeation chromatographic columns and their molar cyclization equilibrium constants were compared with the corresponding theoretical values predicted by the Jacobson–Stockmayer theory as well as those obtained previously for undiluted PDA ring-chain equilibrates. Copyright © 1996 Elsevier Science Ltd.

(Keywords: cyclic polyester; gel permeation chromatography; molar cyclization equilibrium constant)

INTRODUCTION

In earlier investigations, we demonstrated that undiluted ring-chain equilibration reactions of two aliphatic polyesters and one aromatic polyester yield cyclic oligoesters and we were able to analyse some of these cyclics by gel permeation chromatography (g.p.c.)[1]. Thus, the concentrations of individual cyclics $[CO(CH_2)_4CO.O(CH_2)_{10}O]_x$ (where $x = 1$–5) in undiluted ring-chain equilibrates of poly(decamethylene adipate) (PDA)[2] and of individual cyclics $[CO(CH_2)_2CO.O(CH_2)_3O]_x$ (where $x = 1$–7) in undiluted ring-chain equilibrates of poly(trimethylene succinate)[2] were measured by g.p.c., as were the concentrations of individual cyclics $[COC_6H_4CO.O(CH_2)_2O]_x$ (where $x = 3$–9) in ring-chain equilibrates of poly(ethylene terephthalate) (PET)[3].

This paper describes how cyclic oligo- and polyesters can be prepared in high yields by carrying out ring-chain transesterification reactions in the presence of large amounts of solvent and how all the individual cyclic esters containing up to 200 skeletal bonds can be resolved by g.p.c. using E-type columns manufactured recently by Polymer Laboratories Ltd. For such reactions the approach to full equilibration may be slow, but at all stages the cyclics are well separated from the relatively high molar mass chain species that are formed, so the cyclics can be extracted from the reaction products and obtained virtually free of chain species. This contrasts with some polymer-supported reactions, where cyclic esters were produced together with some of the corresponding chain species[4] and where pairs of rings and chains of similar molar mass cannot be separated by the g.p.c. methods currently available[5].

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EXPERIMENTAL

Materials

Dimethyl adipate and 1,10-decanediol were obtained from Fluka Chemika Ltd. The catalyst used in the reactions was tetraisopropyl orthotitanate and it was also obtained from Fluka Chemika. All of the above reagents were used as received.

Preparation of poly(decamethylene adipate) (PDA)

PDA was prepared by a polymerization reaction between dimethyl adipate and 1,10-decanediol. Dimethyl adipate and 1,10-decanediol were added in equimolar proportions (1.5 mol) to a four-necked reaction kettle, which was equipped with an over stirrer, a thermometer and a distillation head. The reaction kettle was purged with dry nitrogen and the contents raised to a temperature of 100°C with stirring to establish thorough mixing and melting of the monomers. The catalyst tetraisopropyl orthotitanate (0.5 wt%) was then added and the temperature raised to 150°C for 12 h, during which time methanol was evolved and distilled off. The temperature was raised to 200°C for 4 h to expel most of the methanol. The reaction mixture was then held at 140°C for a further 12 h and the contents of the kettle were allowed to cool to room temperature under a nitrogen atmosphere.

Preparation of cyclic PDA by solution transesterification

To encourage the formation of cyclic PDA, the high molar mass (predominately chain) polyester (obtained from the melt polymerization described above) was refluxed in dilute solution with further catalyst. The solution transesterification reaction was performed several times with approximately 25 g portions of PDA dissolved in chlorobenzene for polymer/solvent dilution ratios (by weight) of 1/6, 1/10, 1/20, 1/30 and 1/40. The solutions were refluxed at 130°C in the presence of catalyst (0.5 wt% with respect to polymer) for 72 h. The products were collected by distilling off the solvent by rotary evaporation.

The progress of the reaction for the 1/40 polymer/solvent ratio reaction was monitored by removing samples at regular intervals (0, 1, 2, 20, 44 and 72 h and 5 days). Each sample was rotary evaporated to dryness and then analysed by g.p.c.

Extraction of cyclics

The cyclic components from the melt polymerization and the solution transesterification reactions were extracted using a mixture of diethylether and petroleum ether (boiling point range 40–60°C). Each polyester sample was dissolved in twice its weight of chloroform and poured into a 4/1 mixture of diethylether/petroleum ether maintained at 0°C in an ice bath. On addition the non-cyclic product immediately precipitated from solution. The ratio of chloroform solution to ether mixture was adjusted to 1/6 by volume and held at 0°C for 1 h. The soluble cyclic product was collected by filtration and then distilling off the solvent using a rotary evaporator.

Gel permeation chromatography (g.p.c.)

The polyester products and cyclic extracts were analysed using a Knauer GPC instrument, 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}.

Nuclear magnetic resonance (n.m.r.) spectroscopy

^{1}H n.m.r. spectra were obtained on a JOEL 270 MHz spectrometer, using deuterated chloroform as the solvent.

RESULTS AND DISCUSSION

Ring-chain reactions

The products from the melt polymerization and ring-chain transesterification reactions were analysed by g.p.c. using the four 3 μm mixed-E columns and by n.m.r. spectroscopy. The concentrations of the resolved cyclic species were determined by peak area calculations using the GPC Logical software supplied by Polymer Laboratories.

G.p.c. of the melt polymerized PDA showed that high molar mass polymer (M_n = *ca.* 3 × 10^4) had been produced with only small amounts of cyclic oligomers (*ca.* 2.5 wt% as assessed by g.p.c.). The presence of large volumes of solvent (chlorobenzene) in the transesterification had a large effect on the quantity of cyclic species obtained. For dilutions of 1/6, 1/10, 1/20, 1/30 and 1/40 (ratio of weight of polymer to weight of solvent) the yield of cyclic product was estimated by g.p.c. to be 9.5, 10.2, 46.0, 67.5 and 71.9 wt%, respectively. The last peak to elute from the g.p.c. was assigned to the cyclic monomer, an assignment verified by calculated molar mass averages. For dilutions greater than 1/30 cyclics with up to eleven repeat units (198 skeletal bonds) were completely resolved (see *Figure 1*).

Extracts from the ring-chain transesterification reactions using diethyl ether/petroleum ether mixtures demonstrated that samples of polyester rings could be obtained in good yield by this method. G.p.c. analysis of these extracts showed that the cyclics were obtained almost completely free from chain material and that cyclic products could be identified up to eight repeat

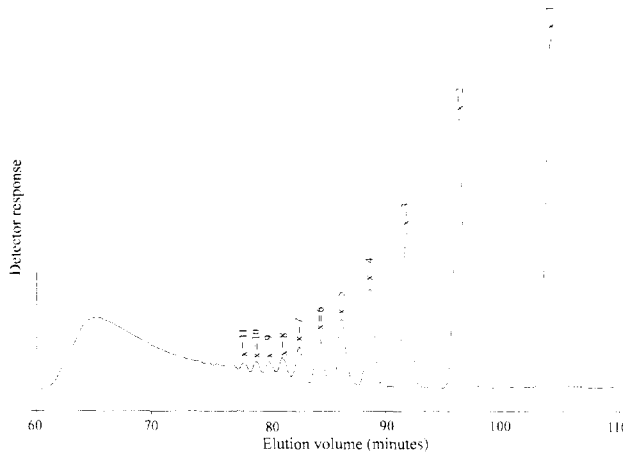

Figure 1 Gel permeation chromatogram of a PDA equilibrate, 1:30 dilution (wt of polymer : wt of solvent), 72 h reaction time, chlorobenzene as the solvent showing cyclics $[CO(CH_2)_4COO(CH_2)_{10}O]_x$

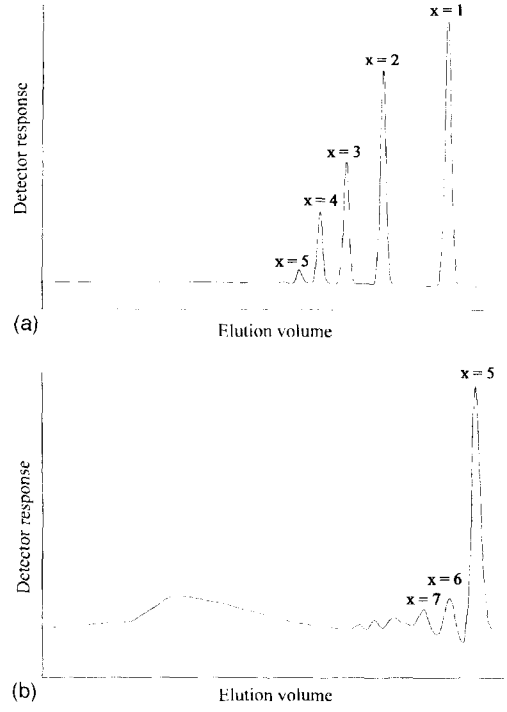

Figure 2 Gel permeation chromatogram of an extracted PDA equilibrate, 1:30 dilution (wt of polymer : wt of solvent), 72 h reaction time, chlorobenzene as the solvent. (a) Cyclic extract showing x-mers in the range 1–5; (b) magnified cyclic extract showing x-mers up to $x = 7$

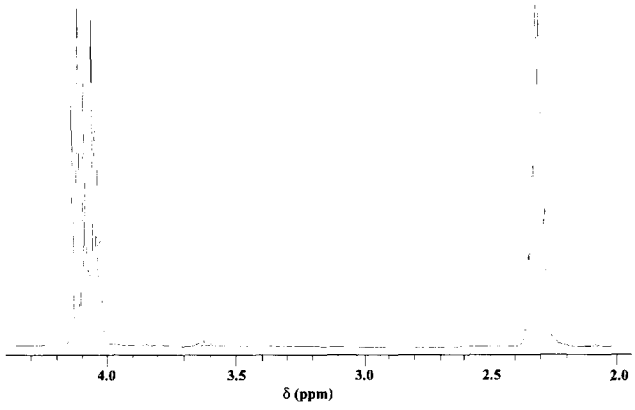

Figure 3 270 MHz ^{1}H n.m.r. spectrum for the extracted PDA cyclics showing responses from the cyclics at $\delta = 4.1$ and $\delta = 2.3$ and the very small response for chain species centred at $\delta = 3.6$

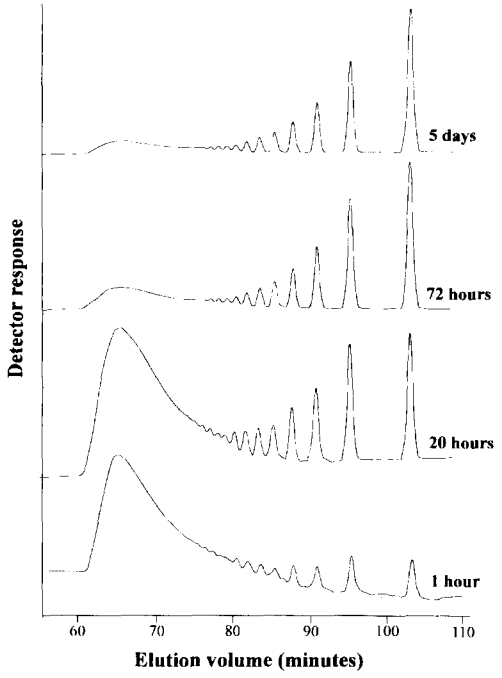

Figure 4 Gel permeation chromatogram showing growth of the PDA cyclic component as a function of time; 1:40 dilution (wt of polymer : wt of solvent), chlorobenzene as the solvent

units (144 skeletal bonds, see *Figure 2*). N.m.r. spectroscopy confirmed the presence of chain polyester end groups but only in very small quantities (see *Figure 3*).

Ring-chain equilibrates

The solution transesterification reaction of PDA with a ratio of weight of polymer to weight of solvent of 1/40 was monitored by removing samples at intervals. The g.p.c. showed that cyclic products were formed early on in the reaction. For example, after 1 h cyclics comprise over 12 wt% of the total product and most of the cyclics are formed after 72 h (72 wt% as determined by g.p.c.). Further refluxing only marginally improves the yield of cyclic polyesters so that after 5 days they make up 79 wt% of the total product. Nonetheless, such high yields would be of considerable advantage when preparative g.p.c. is used with the products. The growth of cyclics in the reactions is illustrated in *Figure 4*, which

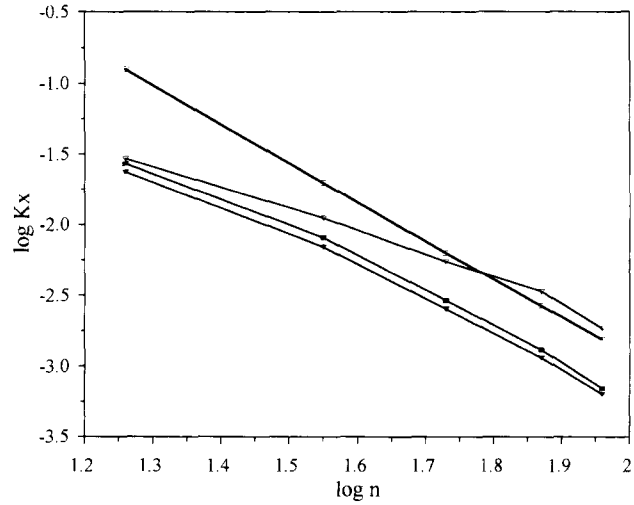

Figure 5 Molar cyclization equilibrium constants plotted as $\log_{10} K_x$ against $\log_{10} n$ where n represents the number of skeletal bonds in the cyclics M_x (–□– theory; –▽– undiluted equilibrate; –■– 5 days (solution); –▼– 12 days (solution) (see text)

shows the ring and chain product distributions at intervals of 1, 20 and 72 h and for 5 days. These studies show that ring-chain equilibrium has been established after 5 days.

Ring-chain equilibria in the PDA system may be represented as follows

$$-M_y- \rightleftharpoons -M_{y-x}- + +M_x \qquad (1)$$

where $-M_y-$ and $-M_{y-x}-$ are chain species, and M_x are the x-meric cyclic species formed in the reactions. The equilibria are not affected by the nature of the end-groups involved in the reactions, which may differ from catalyst to catalyst.

The molar cyclization equilibrium constants K_x (units of mol l^{-1}) for the individual cyclics can be expressed as follows

$$K_x = \frac{[-M_{y-x}-][M_x]}{[-M_y-]} \qquad (2)$$

For these polyester reactions, there should be a most probable distribution of chain lengths[6] in the acyclic part of the polymer so that a Flory or most probable distribution would apply and so

$$K_x = \frac{[M_x]}{p^x} \qquad (3)$$

where p represents the extent of reaction of functional groups in the chain polymer. For the ring-chain equilibrates established in this work, the number average mass of the chain polymer was estimated to be *ca* 3×10^4, p was calculated to be 0.991 using Flory's relationships[6] and K_x values for the cyclics were computed accordingly.

Molar cyclization equilibrium constants K_x calculated using equation (3) are shown for the solution transesterification reactions (after 5 and 12 days). The corresponding values determined for the undiluted ring-chain equilibration reaction of PDA by Jones *et al.*[2] are also shown for purposes of comparison (*Figure 5*).

The experimental K_x values for the solution transesterification reactions are also compared with theoretical

values in *Figure 5*. The latter were calculated using the Jacobson–Stockmayer expression[8,9]

$$K_x = \left(\frac{3}{2\pi\langle r_x^2\rangle_0}\right)^{\frac{3}{2}}\left(\frac{1}{N_A\sigma_{Rx}}\right) \quad (4)$$

where $\langle r_x^2\rangle_0$ represents the mean-square end-to-end distances of x-meric chains unperturbed by excluded volume effects, N_A is the Avogadro constant and σ_{Rx} is the symmetry number representing the number of skeletal bonds that can open in the reverse reaction of equation (1) (here $\sigma_{Rx} = 2x$). In the derivation of equation (4), chains corresponding to rings were assumed to be in random-coil conformations and to obey Gaussian statistics. Values of $\langle r_x^2\rangle_0$ required for equation (4) were computed previously[2] using the rotational isomeric state model of Flory and Williams[10,11] at the temperature of the undiluted PDA ring-chain equilibrate (423 K). Although the experimental K_x for the solution ring-chain equilibria are all lower than the theoretical values over the range shown in *Figure 5*, the characteristic slope of log K_x vs log n of *ca* −2.5 is observed from $x = 2$ as would be expected from equation (4)[12]. The lower K_x values are thought to be related to the fact that chlorobenzene at 130°C is not a θ-solvent for the polymer and there may be specific solvent effects similar to those reported by Flory *et al.* for the poly(dimethylsiloxane) system[13]. The concentrations of chain species with up to $x = 12$ in the products were estimated to be in much smaller concentrations than the cyclics by using Flory's relationship[6] for the weight fraction of x-meric chains.

$$W_x = x(1-p)^2p^{x-1} \quad (5)$$

This is in agreement with the n.m.r. spectroscopic evidence discussed previously.

CONCLUDING REMARKS

The present studies have demonstrated that large cyclic esters with 18–198 skeletal bonds can be prepared in high yields, virtually free of chain species, by solution ring-chain equilibration reactions and can all be analysed by gel permeation chromatography using the new E-type columns manufactured by Polymer Laboratories; which give better resolution for low molar mass polymers and oligomers than their predecessors. It should now be possible to obtain sharp fractions and even individual compounds of the polyester system by the latest preparative g.p.c. methods. Such compounds cannot be prepared any other way. Further investigations of this PDA system and related polyester systems are in progress to explore the conformational characteristics of the chain molecules, to characterize new cyclic populations and to prepare fractions and individual compounds for fundamental investigations of their properties.

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