

Cyclic polyesters: 5. Cyclics prepared by poly(decamethylene terephthalate) ring-chain reactions

S. C. Hamilton and J. A. Semlyen*

Department of Chemistry, University of York, Heslington, Yorks YO1 5DD, UK

(Received 10 May 1996; revised 26 June 1996)

Cyclic oligomers of poly(decamethylene terephthalate) (PDT) were prepared successfully and cleanly from a ring-chain equilibrium reaction in dilute solution of chlorobenzene. A variety of catalysts were investigated for this purpose. The reactions were monitored up to equilibrium and the molar cyclization equilibrium constants K_x deduced. Satisfactory yields of cyclics $[\text{O}(\text{CH}_2)_{10}\text{OCO C}_6\text{H}_4\text{CO}]_x$ were obtained, together with a higher molar mass linear polymer. Mass spectroscopic investigation showed that no monomeric ring was formed in the PDT reaction. The individual cyclics with $x = 2$ –14 corresponding to 36–252 skeletal bonds were completely resolved using PL-gel mixed-E gel permeation chromatographic columns. The lower mass cyclics ($x = 2$ –5) were cleanly extracted and then characterized. The yield of cyclics in ring-chain equilibria corresponding to a solvent/polymer dilution ratio of 30/1, 60/1 and 100/1 were *ca* 11%, *ca* 30% and *ca* 50%, respectively. The K_x values for PDT cyclics were used to compare the statistical conformations of the corresponding PDT chains in chlorobenzene with an aliphatic polyester, poly(decamethylene adipate), which was studied previously. © 1997 Elsevier Science Ltd. All rights reserved.

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

INTRODUCTION

The conformational behaviour or chain ‘flexibility’ of polymers is one of the most important factors in influencing the properties of the polymers. The conformations of polymer chains in dilute solution can be investigated using a variety of techniques including laser light scattering, small angle neutron scattering, viscometry and dipole moment measurements¹. Considerable progress has been made in the interpretation of the average conformations of linear polymers under θ point conditions using rotational isomeric state models^{1,2} and molecular modelling techniques, despite the relative sparsity of detailed experimental information and data available in the literature.

A most effective method of investigating the conformations of polymer chains is by the measurement of individual cyclic concentrations in ring-chain equilibrium reactions, which we have been developing in our laboratory^{3–5}. One of the aims of our work on cyclic polymers has been to apply this approach to a wide range of polymer systems, including polysiloxanes, polyesters, polyethers, polyamides and polyphosphates^{3–6}. For example, the statistical conformations of siloxane chains $-\text{R}(\text{CH}_3)_2\text{SiO}-$ (where $\text{R} = \text{H}, \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, \text{CF}_3\text{CH}_2\text{CH}_2, \text{CH}_2 = \text{CH}$ and C_6H_5) were all measured in our laboratory using the equilibrium cyclic concentration method, and a direct comparison of the various chain dimensions was carried out^{5–8}.

The advantages of the equilibrium cyclic concentration

method for characterizing the statistical conformations of oligomeric and polymeric chain molecules is that detailed information can be obtained over a range of chain lengths and in a variety of different environments. Such information is most useful when the statistical conformations of the linear polymer are interpreted theoretically in terms of molecular structure^{1,2}. Following our work on polysiloxane systems, we have now begun a general investigation of the concentration of cyclics in polyester systems, to be followed by an investigation of the physical and topological properties of the large ring molecules.

In this paper, we examine the conformational consequences of phenyl groups when they are inserted in an aliphatic polyester chain molecule, by comparing the statistical conformations of poly(decamethylene terephthalate) (PDT) with the already published data for poly(decamethylene adipate) (PDA)⁹. The terephthalate residue is present in commercial poly(ethylene terephthalate) and poly(butylene terephthalate), which are also currently under investigation in our laboratory.

Here we demonstrate that (i) ring-chain equilibria can be established in the PDT system provided a suitable catalyst is used and that (ii) high dilution can result in good yields of pure cyclics, so that preparative gel permeation chromatography (g.p.c.) could be used to obtain sharp fractions of these ring compounds on a substantial scale. Since large cyclic molecules have a different topology from long chain molecules, they have some quite different properties¹⁰, e.g. the capacity to be entrapped in networks¹¹ and form catenated polymers¹².

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Dimethyl terephthalate and 1,10-decandiol were obtained from Fluka Chemicals. The catalysts used were tetraisopropyl orthotitanate, zinc acetate and dibutyltin bis-(2-hexanoate), and these were obtained from Aldrich. All of the above reagents were used as received.

Preparation of PDT

PDT was prepared by a polymerization reaction between dimethyl terephthalate and 1,10-decandiol. Dimethyl terephthalate and 1,10-decandiol were added in equimolar proportions to a four-necked reaction vessel, which was equipped with an overhead stirrer, a thermometer and a distillation head. The reaction vessel was purged with dry nitrogen, and the temperature was raised to 140°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 was raised to 190°C for 48 h *in vacuo* to remove methanol from the system. The products were then allowed to cool to room temperature under a nitrogen atmosphere. The molar mass of the polymer was found to be *ca* 40 000 by g.p.c.

Preparation of cyclic PDT by solution transesterification

The high mass linear PDT obtained as described above was refluxed in a dilute solution of chlorobenzene (30/1 w/w) with further catalyst (0.5% w/w). The transesterification reaction was performed three times with approximately 10 g of PDT dissolved in chlorobenzene, each time with a different catalyst. The catalysts used were tetraisopropyl orthotitanate, zinc acetate and dibutyltin bis-(2-hexanoate). The progress of each reaction was monitored by sampling at regular intervals, drying the products down by rotary evaporation and then analysing by g.p.c. From the data obtained the molar cyclization equilibrium constants for the cyclics in each system at equilibrium were deduced.

A further study was carried out involving ring-chain equilibrium reactions at different dilutions of 30/1, 60/1 and 100/1 using 0.5% (w/w) zinc acetate, which was found to be the most suitable catalyst.

Extraction of cyclics

The cyclics from the ring-chain equilibrium reaction were extracted using a mixture of petroleum ethers (boiling point range 40–60°C and 60–80°C). Each polyester sample was dissolved in three times its weight of chloroform and poured into a cold (0°C) 1:1 mixture of the two petroleum ethers. On the addition, the linears immediately precipitated from solution. The ratio of chloroform solution to the petroleum ether mixture was 1:8. The soluble cyclic product was collected by filtration and then rotary evaporated and vacuum pumped to dryness.

Gel permeation chromatography

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. 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.

Table 1 Variation in cyclic yield of PDT from the ring-chain equilibrium reaction with different catalysts

Catalyst in 30/1 dilution reaction	Yield of cyclics (% of total product)
Tetraisopropyl orthotitanate	3
Dibutyltin bis-(2-hexanoate)	8
Zinc acetate	11

Table 2 Effect of dilution in PDT ring chain equilibrium reaction using a zinc acetate catalyst on the yield of cyclics

Chlorobenzene dilution	Yield of cyclics (% of total product)	Time taken to reach equilibrium (days)
30/1	11	6
60/1	30	14
100/1	50	30

Nuclear magnetic resonance (n.m.r.)

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

Mass spectroscopy

FAB mass spectra were obtained using a NOBA matrix and CHCl₃ 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. as described in the previous section. The results are shown in *Figure 1*. The concentrations of the resolved cyclic species were determined by peak area estimates using the GPC Logical software supplied by Polymer Laboratories, which assumes that all the cyclic species give similar responses using the refractive index detector. Data relating to the reaction products at equilibrium are given in *Tables 1* and *2*. *Table 1* shows that zinc acetate is the most effective catalyst for the PDT system, yielding *ca* 11% cyclics in chlorobenzene/polymer (30/1) dilution. This is compared with 8% for dibutyltin bis-(2-hexanoate) and 3% for tetraisopropyl orthotitanate, both under the same conditions. *Table 2* shows that the cyclic concentration in the equilibrate rises with increasing dilution, with *ca* 11% at 30/1 dilution, *ca* 30% at 60/1 dilution and *ca* 50% at 100/1 dilution.

Extraction and characterization of cyclic oligomers

Following the extraction of the cyclics described in the Experimental section, the cyclic extracts were each analysed by g.p.c. One of the resulting chromatograms is shown in *Figure 2*. This was obtained from the zinc acetate catalysed 60/1 dilution reaction, but is representative of all the systems. It shows a complete absence of linear species.

The mass spectrum of one of the cyclic extracts is shown in *Figure 3*, confirming that no monomeric ring is formed, and the product consists of dimer and higher cyclic oligomers. It can easily be seen that there are peaks corresponding to [M]⁺, [MNa]⁺ and [M-H₂O]⁺ for each species.

The ¹H n.m.r. spectra of the cyclic oligomers shows no evidence of end groups. An example is displayed in

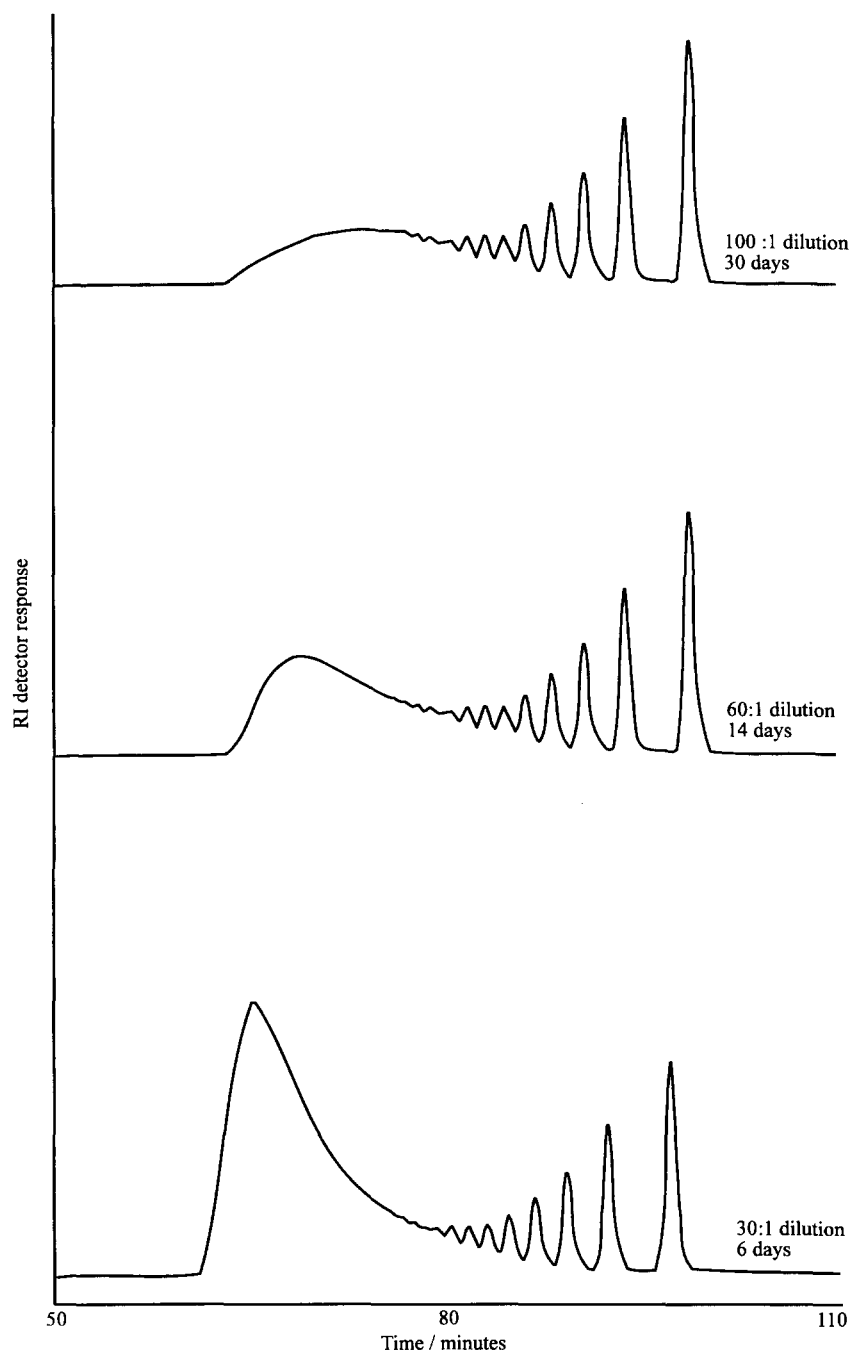


Figure 1 G.p.c. trace of poly(decamethylene terephthalate) (PDT) ring-chain equilibrium reaction products in 30/1, 60/1 and 100/1 chlorobenzene-PDT dilutions

Figure 4b, where it is compared with the corresponding spectrum for the linears produced in the reaction in Figure 4a.

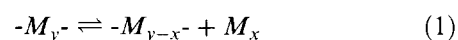
These characterization methods show that the PDT system produces large cyclic species uncontaminated by linear oligomers. The cyclics described in this paper could be used for ring opening polymerization reactions, and for topological studies, e.g. by entrapping them into networks^{13,14}. They could also be divided into sharp fractions by preparative g.p.c. to give materials suitable for further chemical and physical investigations.

Analysis of results

The investigations described here have led to the determination of the molar cyclization equilibrium

constants of the cyclics $[\text{O}(\text{CH}_2)_{10}\text{OCOC}_6\text{H}_4\text{CO}]_x$ with $x = 2-14$. This was done from g.p.c. tracings by analysing peak areas of individual cyclic species, as well as the area of the whole reaction products by the Logical GPC software supplied by Polymer Laboratories. Equation (3) was then used to determine K_x values, using the Flory relationship in equation (5), assuming similar peak responses for the individual oligomers.

Ring chain equilibria in this system may be represented as follows:



where $-M_y^-$ and $-M_{y-x}^-$ represent the chain species and M_x represents the x -meric cyclic compounds formed in the reactions. The molar cyclization equilibrium

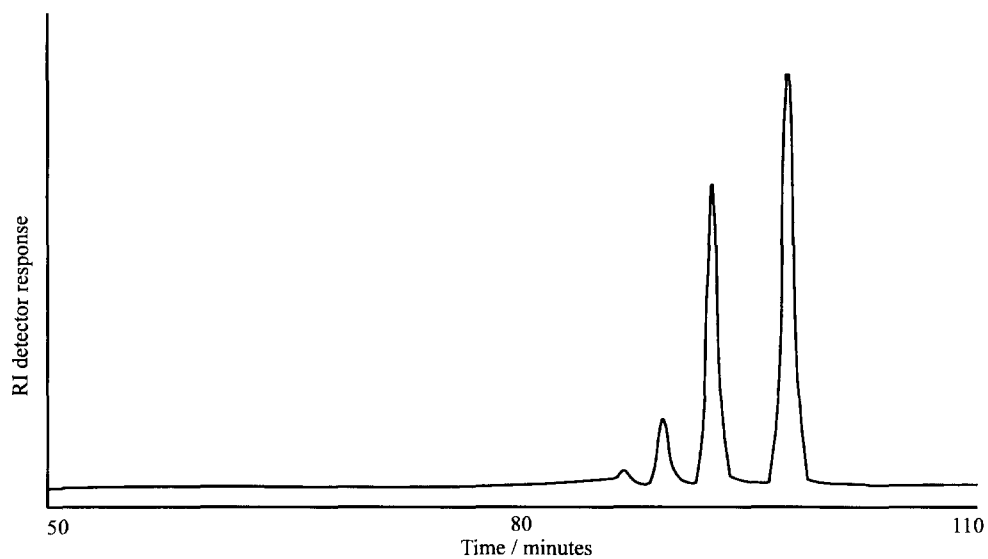


Figure 2 G.p.c. chromatogram of cyclics extracted from the PDT ring-chain equilibrium reaction products

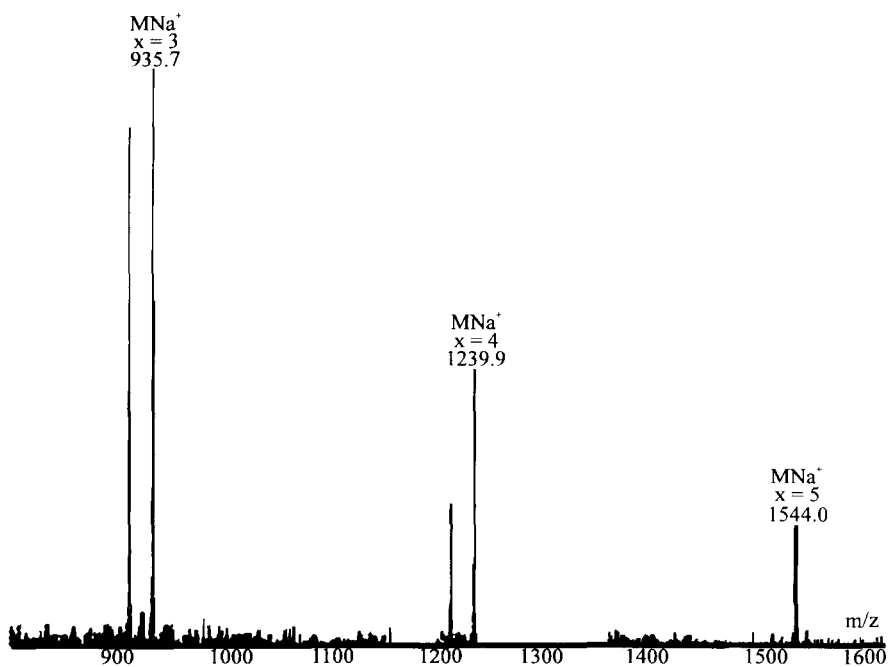
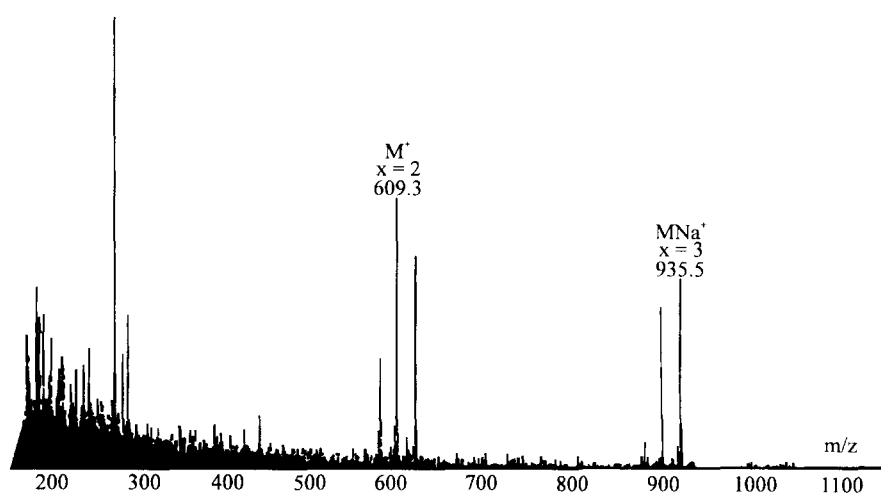


Figure 3 FAB mass spectrum of cyclics extracted from the PDT ring-chain equilibrium reaction products

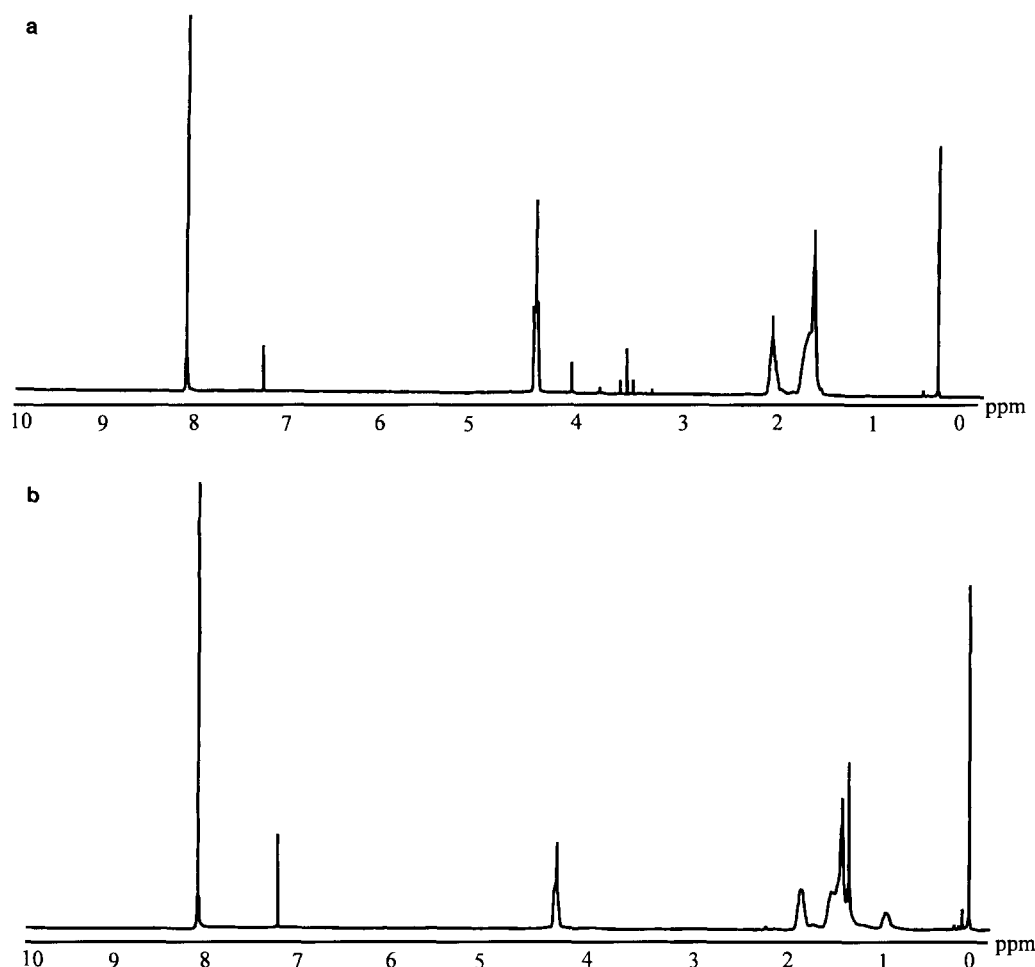


Figure 4 ^1H n.m.r. spectra of the PDT ring-chain equilibrium reaction products, and of the cyclics extracted from the PDT ring-chain equilibrium reaction products

constants K_x (mol l^{-1}) for the individual cyclics are given by

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

For these polyester reactions, there is a Gaussian distribution of chain lengths for the linears and a Flory distribution would apply, so that

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

where p represents the extent of reaction of functional groups in the chain polymer¹⁵, and the weight fraction of the x -meric chains is given by

$$W_x = x(1-p)^2 p^{x-1} \quad (4)$$

where p is given by the relationship¹⁵:

$$p = 1 - \frac{M_0}{M_n} \quad (5)$$

The number average molar mass M_n of the linear polymers produced in the ring-chain equilibrium reaction were estimated by g.p.c. to be greater than 30 000, so that even in the region $x = 14$, the concentrations of chain species are much smaller than those of the rings and can be neglected.

The Jacobson–Stockmayer theory^{16,17} gives the following expression for the K_x values of large ring molecules

corresponding to chains in random coil conformations obeying Gaussian statistics:

$$K_x = \left(\frac{3}{2\pi \langle r_x^2 \rangle_0} \right)^{3/2} \left(\frac{1}{\sigma_{Rx} N_A} \right) \quad (6)$$

Where $\langle r_x^2 \rangle_0$ represents the statistical mechanical mean square values of the end to end distances of the corresponding x -meric open chain molecules, N_A is the Avogadro constant, and σ_{Rx} is a symmetry number corresponding to the number of bonds that can open in the reverse reaction of equation (1)¹⁶.

For polyesters of the type described here $\sigma_{Rx} = 2x$, so the above equation can be written as

$$K_x = \frac{(3/\pi)^{3/2}}{2^{5/2} l^3 C_x^{3/2} n^{3/2} x N_A} \quad (7)$$

where $C_x = \langle r_x^2 \rangle_0 / nl^2$ is a ratio characteristic of an x -meric cyclic with n skeletal bonds.

Plots of the logarithms of the molar cyclization equilibrium constants against the logarithms of the number of skeletal bonds for PDT, together with the corresponding values for the PDA system, are shown in *Figure 5*. Both sets of cyclic oligomers have 18 skeletal bonds per repeat unit, and so can easily be compared. The $\log K_x$ versus $\log n$ plot for PDT gives a mean slope close to -3.0 in the region $n = 32-180$ compared to the Jacobson–Stockmayer¹⁶ limiting value

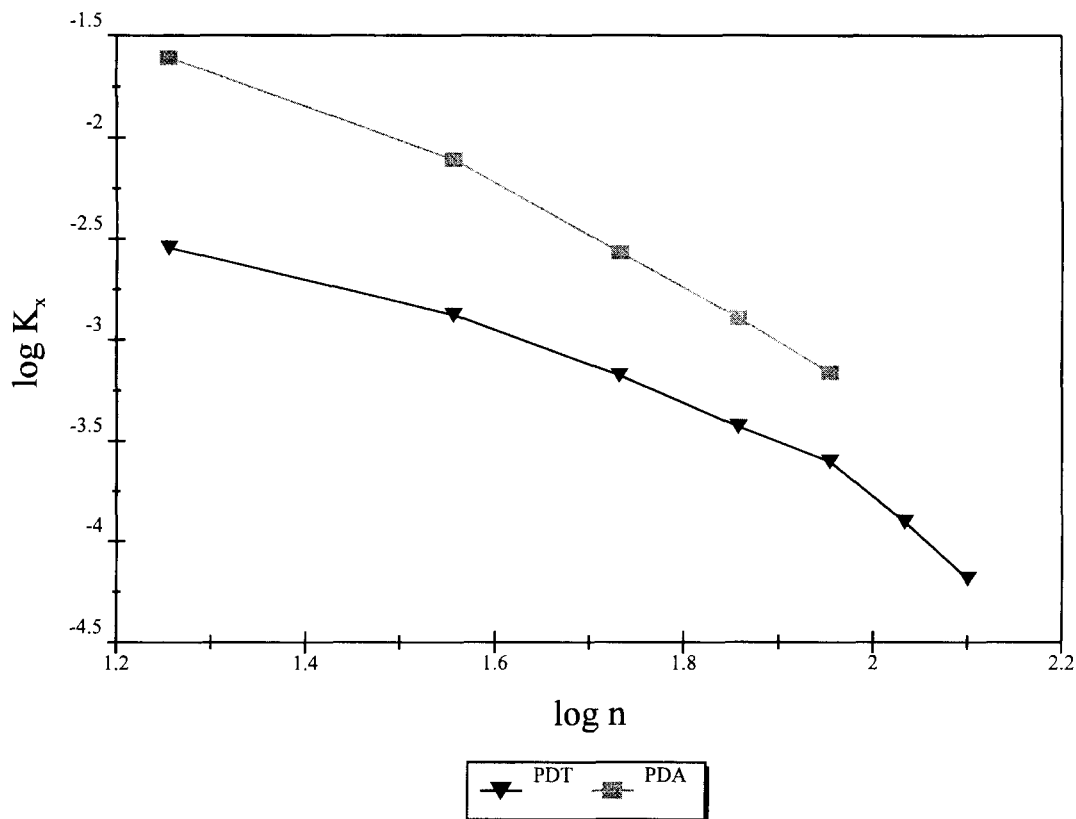


Figure 5 Plot of the logarithm of the molar equilibrium cyclization constant K_x versus the logarithm of the number of skeletal bonds n for PDA and PDT cyclics

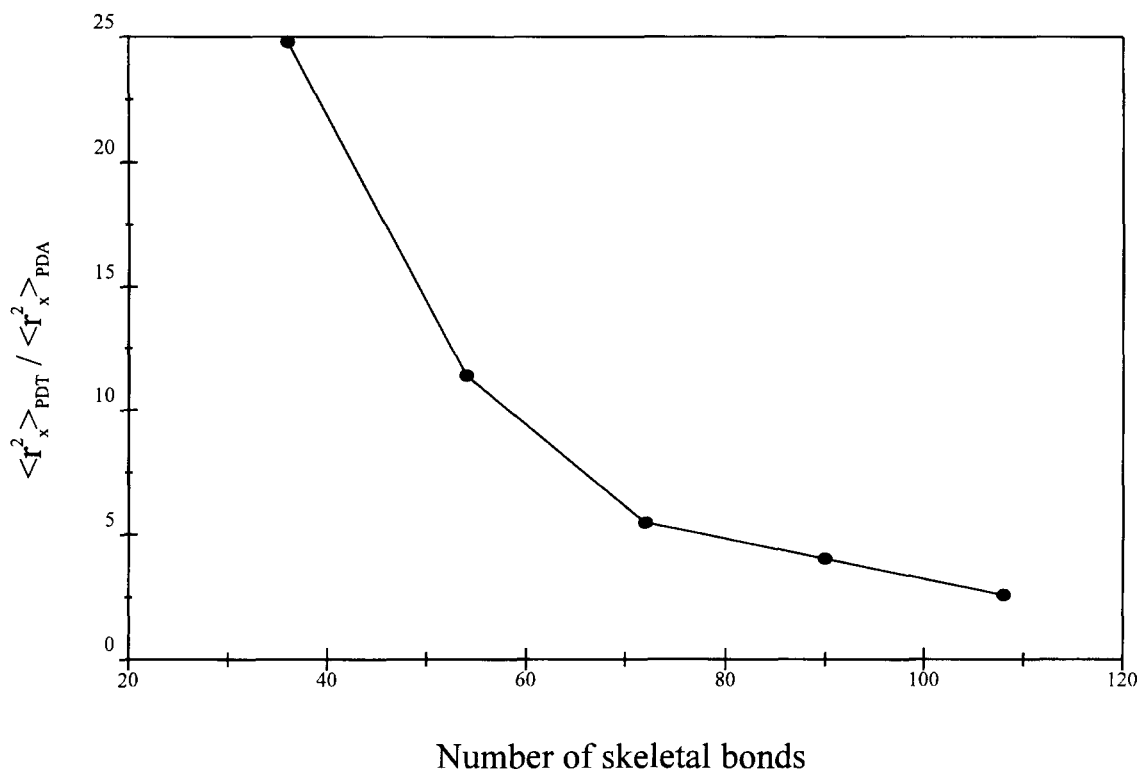


Figure 6 Plot of the ratios of $\langle r_x^2 \rangle_{PDT} / \langle r_x^2 \rangle_{PDA}$ versus the number of skeletal bonds n of linear PDT and PDA chains

of -2.5 (see Figure 5). The higher oligomers are present in much lower concentrations, and hence there is a greater uncertainty in their experimental K_x values.

The data obtained here and in the previous study allow the ratio of the statistical mechanical average of r^2 over

all configurations of the chain $\langle r_x^2 \rangle_{PDT} / \langle r_x^2 \rangle_{PDA}$ to be deduced over the range 36–108 skeletal bonds. The results are shown plotted in Figure 6. The plot shows that the effects of the phenyl groups on the molecular volumes of the lower oligomers are relatively much

greater, particularly for the dimer and the trimer. These effects are much smaller from the tetramer onwards. It is noted that the PDA system yields a monomer, whereas the PDT system does not, as could be expected from molecular modelling studies.

The ratio of $\langle r_x^2 \rangle / nl^2$ for a chain of n bonds for PDT can be deduced from the K_x values using equation (7). It should be noted that this is not a true characteristic ratio as the experiments were carried out in chlorobenzene, which is not a Θ -solvent for the polymer. Some expansion of the chain dimensions would be expected from excluded volume effect and there may be specific solvent effects arising from the halogenated solvent, as described for poly(dimethyl siloxane) by Flory *et al.*¹⁸. The limiting value of $\langle r_x^2 \rangle / nl^2 = 13$ found here is larger than the corresponding ratio of 8 found by Wood *et al.*⁹ for PDA chains in the same solvent. These studies illustrate how measurements of cyclic concentrations in polymeric equilibria can yield detailed information relating to the statistical conformations of the corresponding chain molecules. Further studies of cyclic polyesters are currently in progress in our laboratory.

ACKNOWLEDGEMENTS

The authors would like to thank the EPSRC and Courtaulds Coatings Ltd., Stonegate Lane, Felling, Gateshead, Tyne and Wear, UK, for financial support for this work. We would also like to thank the n.m.r. and mass spectroscopy services at the University of

York, and Dr B. R. Wood for helpful discussions and advice.

REFERENCES

- 1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
- 2 Mattice, W. L. and Sutter, U. W. 'Conformational Theory of Large Molecules', John Wiley, Chichester, New York, 1994
- 3 Semlyen, J. A. and Wood, B. R. *Polym. News* (in press)
- 4 Semlyen, J. A. (Ed.) 'Cyclic Polymers', Elsevier Applied Science, London and New York, 1986
- 5 Clarson, S. J. and Semlyen, J. A. 'Siloxane Polymers', Prentice-Hall, Englewood Cliffs, NJ, 1993
- 6 Semlyen, J. A. 'Studies of Cyclic and Linear Poly(dimethylsiloxanes)', Parts 1–32, *Polymer* 1978–1996
- 7 Wood, B. R., Semlyen, J. A. and Hodge, P. *Polymer* 1994, **35**, 1542
- 8 Semlyen, J. A. and co-workers, 'Cyclic Polysiloxanes', Parts 1–6, *Polymer* 1986–1996
- 9 Wood, B. R., Semlyen, J. A. and Hodge, P. *Polymer* (in press)
- 10 Semlyen, J. A. (Ed.) 'Large Ring Molecules', John Wiley, Chichester, New York (in press)
- 11 Clarson, S. J., Mark, J. E. and Semlyen, J. A. *Polym. Commun.* 1987, **27**, 244
- 12 Wood, B. R., Hodge, P. and Semlyen, J. A. *Polymer* 1993, **34**, 3052
- 13 Garrido, L., Mark, J. E., Clarson, S. J. and Semlyen, J. A. *Polym. Commun.* 1985, **26**, 53, 55
- 14 Wood, B. R., Joyce, S. J., Scrivens, G., Semlyen, J. A., Hodge, P. and O'Dell, R. *Polymer* 1993, **34**, 14, 3059
- 15 Semlyen, J. A. *Adv. Polym. Sci.* 1976, **21**, 43
- 16 Jacobson, H. and Stockmayer, W. H. *J. Chem. Phys.* 1950, **18**, 1600
- 17 Flory, P. J. 'Statistical Mechanics of Chain Molecules', John Wiley, New York, 1969
- 18 Flory, P. J., Crescenzi, V. and Mark, J. E. *J. Am. Chem. Soc.* 1964, **86**, 141