Cyclic polyesters: 2. Topological trapping experiments and theoretical studies

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A topological trapping method was employed to confirm the cyclic nature of the polyester, which was prepared in part 1 using a polymer-supported reagent. It was found that approximately equal amounts of cyclic polyesters and cyclic poly(dimethylsiloxane)s (PDMS) (with comparable molar masses) could be entrapped in PDMS networks. By contrast, under similar conditions, far smaller quantities of a linear polyester were entrapped. The 'sizes' and 'shapes' of cyclic polyesters were compared with those of cyclic PDMS using a rotational isomeric state model (RISM). Molecular modelling using Quanta and CHARMm programs showed that cyclic polyesters adopted approximately circular conformations when they were subject to energy minimization.

(Keywords: cyclic polymers; polyesters; molecular modelling)

INTRODUCTION

In part 1[1], we reported the preparation of cyclic oligomeric and polymeric esters based on the monomeric repeat unit $[(CH_2)_{10}CO.O]$, using the technique of polymer-supported synthesis. In this paper we show how topological trapping experiments confirm the cyclic nature of the polyester.

Topological trapping results from the fact that cyclic polymers become threaded onto network polymer chains before crosslinking. The crosslinking process causes the threaded cyclic molecules to become permanently trapped within the resulting polymer network. The trapped cyclic polymer cannot then be removed from the network without breaking chemical bonds. In the trapping process no chemical bonds are formed between the cyclic polymer and the polymer network[2].

The topological trapping technique has been established for cyclic poly(dimethylsiloxane) (PDMS)[2–5] in both PDMS and poly(2,6-dimethyl-1,4-phenylene oxide)[6,7] networks. This paper describes the first application of the technique of topological trapping to confirm the cyclic nature of a polymer.

The experimental topological trapping data for cyclic PDMS and cyclic polyester in PDMS networks are compared later in the paper with calculated 'sizes' and 'shapes' of the cyclic polymers and with the results of molecular modelling studies.

EXPERIMENTAL

Cyclic PDMS

The cyclic PDMS used in these experiments were prepared at the University of York and fractions with narrow molar mass distributions were obtained by preparative g.p.c.[8].

Cyclic polyester

The cyclic polyester was prepared by the technique of polymer-supported synthesis as described in part 1[1]. The polymer was fractionated using preparative g.p.c. and characterized by analytical g.p.c., n.m.r. spectroscopy and fast atom bombardment (f.a.b.) mass spectrometry.

Linear polyester

Linear polyester (which would be expected to contain small quantities of cyclics) based upon the monomeric repeat unit $[(CH_2)_{10}CO.O]$ was prepared at the University of Manchester using the following method: 11-bromoundecanoic acid was dissolved in chloroform to give a solution concentration of ≈ 0.8 M. Four drops of a 1% phenolphthalein indicator solution (in isopropanol) were added. Then 95% of a molar equivalent of aqueous tetrabutylammonium hydroxide (40 wt%) was added instantly. The remaining 5% was added dropwise until the characteristic pink end-point was reached. The resulting two-phase mixture was stirred with heating (343 K) for 2.5 h, after which time the oligomers were of suitable molar mass. The oligomers were then precipitated as a fine white powder by adding the two-layered aqueous/chloroform mixture to an excess of acidified methanol (the methanol contained sufficient hydrochloric acid to protonate all acid end groups). The oligoester was characterized at the University of York using analytical g.p.c. and was found to have a molar mass of ≈ 4000. The g.p.c. instrument was calibrated using the universal calibration procedure employing polystyrene molar mass standards. Preparative g.p.c. was used to obtain sharp molar mass fractions. Two fractions with molar masses comparable to the cyclic polyesters were used in the topological trapping study.

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Preparation of the polymer networks

The polymer networks were prepared by the cross-linking reaction between hydroxyl terminated linear PDMS ($M_n \approx 18\,000$) and tetraethylorthosilicate (TEOS). The reaction was catalysed by tin(II) ethylhexanoate with toluene as the solvent. Solutions containing the hydroxyl terminated linear PDMS (4 g), TEOS (0.025 g) and the polymers to be trapped were prepared using toluene as the solvent. The resulting solutions were allowed to stand for ≈12 h and then mechanically shaken for an additional 4 h. The catalyst (0.04 g) was added and again the solutions were shaken for 20 min, at which time the viscosity began to increase. After an additional standing time of 2 min, to allow air bubbles to escape, the solutions were poured into poly(tetrafluoroethylene) covered moulds (60 mm × 60 mm × 3 mm). The specimens were allowed to stand for 5 days at room temperature and pressure, after which time they were transferred to a vacuum oven for 7 days and dried under reduced pressure at a temperature of 325 K.

A blank specimen was also prepared using the above conditions with no cyclic polymer added. In addition to specimens containing cyclic polyester and cyclic PDMS, specimens were also prepared in the presence of linear polyester.

After the specimens were dried, allowed to cool and removed from their moulds, they were divided in two and weighed. The untrapped polymer species were then extracted by swelling and deswelling in toluene/methanol mixtures at room temperature for 14 days, i.e. for periods of 3 days each with 25, 50 and 75% toluene and then finally 5 days in 100% toluene. The specimens were then dried in a vacuum oven under reduced pressure at a temperature of 325 K for ≈48 h and then weighed at intervals to constant weight. From the corresponding weight losses and after allowance for the weight loss due to the PDMS network (from the blank specimens) the average weight loss assuming all untrapped material had been extracted, was then determined for each specimen.

RESULTS AND DISCUSSION

Topological trapping

The quantities of polymer retained by the PDMS network specimens were determined by weight loss measurements (*Table 1*). The polyester rings appear to have been trapped in the network polymer in comparable amounts to those of the PDMS rings; whereas with the linear polyesters only very small amounts of material had been retained by the network. Thus, there is convincing evidence that the polyesters formed by the method of polymer-supported synthesis are cyclic in nature. The small amounts of the polyester material found to have been trapped by the polymer network are believed to be small quantities of cyclic species present within the predominantly linear polyesters. The presence of the small cyclic component was shown by f.a.b. mass spectrometry. Such cyclic components would be expected to be formed in the ring-chain polymerization reaction.

Table 1 Topological trapping results showing the amount of polymer retained by the PDMS networks

Polymer	Number average number of skeletal bonds	Polymer trapped (wt%)
Cyclic PDMS	198	48
Cyclic PDMS	276	72
Cyclic polyester	176	27
Cyclic polyester	238	50
Linear polyester	145	1
Linear polyester	210	2

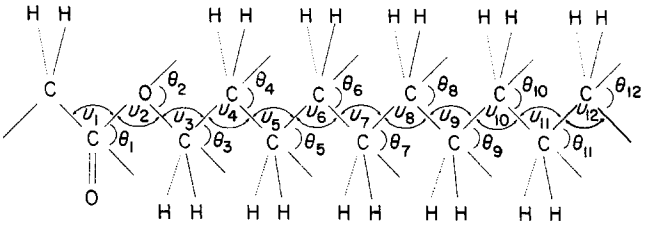

Figure 1 Section of the polyester chain unit

Table 2 Structural parameters for RISM

Bond angles (deg)		Bond lengths (Å)	
θ_1	66	C–CO	1.51
θ_2	67	CO–O	1.33
θ_3	70	O–CH_2	1.44
$\theta_4 = \theta_{5-12}$	68	CH_2–CH_2	1.53

Size and shape of the cyclic and linear polymers

In order to obtain a better understanding of the entrapment of cyclic polyesters in polymeric networks a computer simulation based on a rotational isomeric state model (RISM) was set up, based on the general RISM for aliphatic polyesters, as described by Flory and Williams[9] and Jones *et al.*[10]. A section of the polyesters chain repeat unit in the all-*trans* conformation is shown in *Figure 1*. The structural parameters used in the RISM (bond lengths and bond angles) are given in *Table 2*.

The Flory–Williams model assumes that the ester group adopts a planar *trans* conformation only. The remaining skeletal bonds are assigned rotational states in *trans* ($\phi = 0°$) and *gauche* ($\phi = \pm 120°$) positions. Statistical weight matrices were used to account for interdependent rotations about adjacent pairs of skeletal bonds and the minimized energy conformations were studied at a temperature of 298 K. The corresponding statistical weight matrices used in the RISM are as follows:

$$U_1 = [1]$$

$$U_2 = [1 \quad 0.5 \quad 0.5]$$

$$U_3 = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0.1 \\ 1 & 0.1 & 1 \end{bmatrix}$$

$$U_4 = \begin{bmatrix} 1 & 0.43 & 0.43 \\ 1 & 0.43 & 0.043 \\ 1 & 0.043 & 0.43 \end{bmatrix}$$

$$U_5 = U_6 = U_7 = U_8 = U_9 = U_{10} = \begin{bmatrix} 1 & 0.43 & 0.43 \\ 1 & 0.43 & 0.01462 \\ 1 & 0.01462 & 0.43 \end{bmatrix}$$

$$U_{12} = U_{11} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0.1 \\ 1 & 0.1 & 1 \end{bmatrix}$$

Using the RISM for the chain polyesters, the characteristic ratio $C_\infty = \langle r^2 \rangle_0 / nl^2$ (where n is the number of skeletal bonds of mean square length l) was calculated to be 6.8 at 298 K. This is in line with experimentally determined values due to Knecht and Elias[11], where the characteristic ratios for a number of aliphatic polyesters were found to lie in the range $5.5 < C_\infty < 7.0$ at temperatures from 291 to 308 K[10].

In order to study the 'size' and 'shape' of the linear and cyclic polyesters a Monte Carlo simulation was carried out using the RISM to generate samples of individual conformations of the polymer. These samples give a representation of the total number of conformations defined by the RISM. The Monte Carlo method was used to calculate the radii of gyration of cyclic and linear polyesters in a similar way to that used with polysiloxanes[12,13]. A ring was assumed to be formed when the end-to-end distance r of the corresponding chain was $r \leqslant 3$ Å[14–20]. The 'size' of the polymers was characterized by the radius of gyration $\langle S^2 \rangle$ and by $\langle S^2 \rangle / nl^2$. The 'shape' of the randomly generated polymers was characterized by the x, y and z components of the radius of gyration, i.e. S_x^2, S_y^2 and S_z^2. For every polymer ring or chain generated, these components were sorted such that $S_x^2 \geqslant S_y^2 \geqslant S_z^2$. Using the components of the radii of gyration it is possible to construct an equivalent ellipsoid of uniform density with the same principal moment of inertia as that of the generated polymer, so that:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$$

where a, b and c represent the semi-axes of the equivalent ellipsoid such that $a \geqslant b \geqslant c$. It has been shown[12] that:

$$S^2 = \frac{1}{5}(a^2 + b^2 + c^2)$$

and consequently

$$\frac{S_x^2}{a^2} + \frac{S_y^2}{b^2} + \frac{S_z^2}{c^2} = \frac{1}{5}$$

therefore

$$\frac{\langle S_x^2 \rangle}{\langle a^2 \rangle} + \frac{\langle S_y^2 \rangle}{\langle b^2 \rangle} + \frac{\langle S_z^2 \rangle}{\langle c^2 \rangle} = \frac{1}{5}$$

Consequently the ratio $\langle S_x^2 \rangle : \langle S_y^2 \rangle : \langle S_z^2 \rangle$, i.e. $\langle a^2 \rangle : \langle b^2 \rangle : \langle c^2 \rangle$, can be used to investigate the shape of the generated polymer.

The components of the radius of gyration S_x^2, S_y^2 and S_z^2 were found using the following relationships:

$$S_x^2 = \frac{\sum_{i=1}^{w} (x_i - \bar{x})^2}{w}$$

$$S_y^2 = \frac{\sum_{i=1}^{w} (y_i - \bar{y})^2}{w}$$

$$S_z^2 = \frac{\sum_{i=1}^{w} (z_i - \bar{z})^2}{w}$$

and

$$S^2 = S_x^2 + S_y^2 + S_z^2$$

where x_i, y_i and z_i are the coordinates of the ith polymer segment and w represents the number of skeletal atoms. Many generations of conformations gave the average values $\langle S_x^2 \rangle$, $\langle S_y^2 \rangle$, $\langle S_z^2 \rangle$ and $\langle S^2 \rangle$. The above parameters were determined for cyclic and linear polyesters with the number of repeat units (x) ranging from $1 \leqslant x \leqslant 16$ ($12 \leqslant n \leqslant 192$ skeletal bonds).

Using the computer simulation, cyclic polyesters were generated with a size distribution as shown in *Figure 2*. Here it can be seen that rings with skeletal bonds in the range $24 \leqslant n \leqslant 36$ dominate the size distribution. The calculated mean square radii of gyration $\langle S^2 \rangle$ of the rings and chain polyesters are shown in *Figure 3*. It can be seen that for both the mean square radii of gyration increase linearly with increasing number of repeat units; the rings vary in radii from 7 to 200 Å^2 and the chains 10–400 Å^2 for repeat units over the range $1 \leqslant x \leqslant 16$. It was also shown that the ratio of the mean square radii of gyration for rings and chains $\langle S^2 \rangle_l / \langle S^2 \rangle_r$ was ≈ 2.0 over the range $12 \leqslant n \leqslant 192$ skeletal bonds.

The conformational averages for the principal axes of the equivalent ellipsoids ($\langle a^2 \rangle$, $\langle b^2 \rangle$ and $\langle c^2 \rangle$) for cyclic and linear polyesters with n skeletal bonds over the range

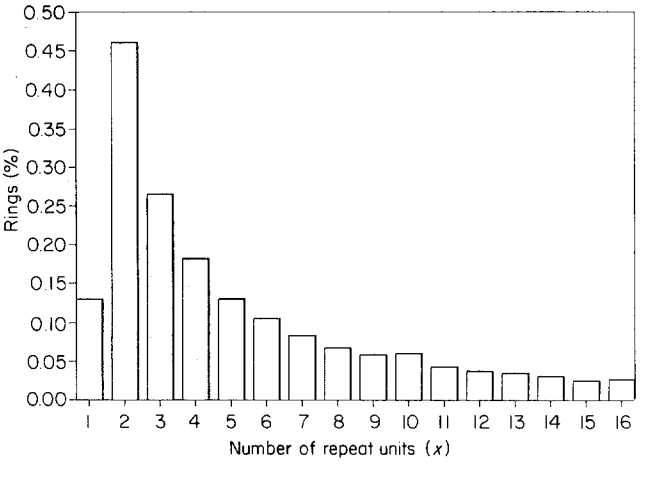

Figure 2 Size distribution for the cyclic polyesters generated using the RISM

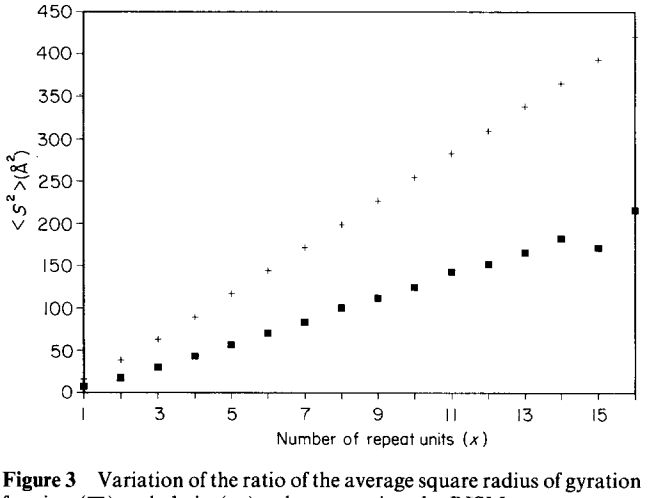

Figure 3 Variation of the ratio of the average square radius of gyration for ring (■) and chain (+) polyesters using the RISM

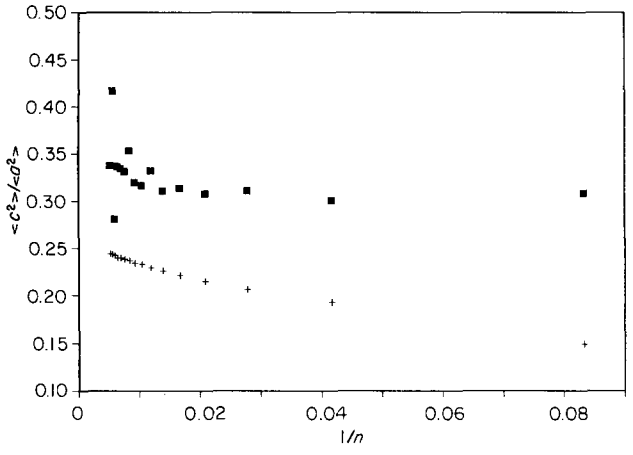

Figure 4 Variation of the ratio of the average square smallest to largest semi-axes for equivalent ellipsoids for ring (■) and chain (+) polyesters generated using the RISM

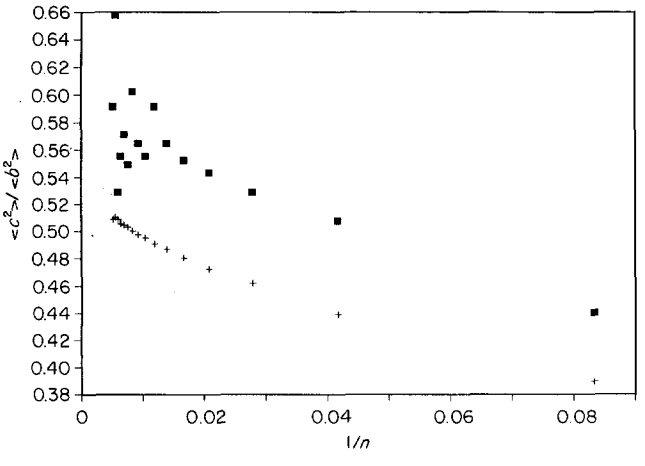

Figure 5 Variation of the ratio of the average square smallest to second largest semi-axes for equivalent ellipsoids for ring (■) and chain (+) polyesters generated using the RISM

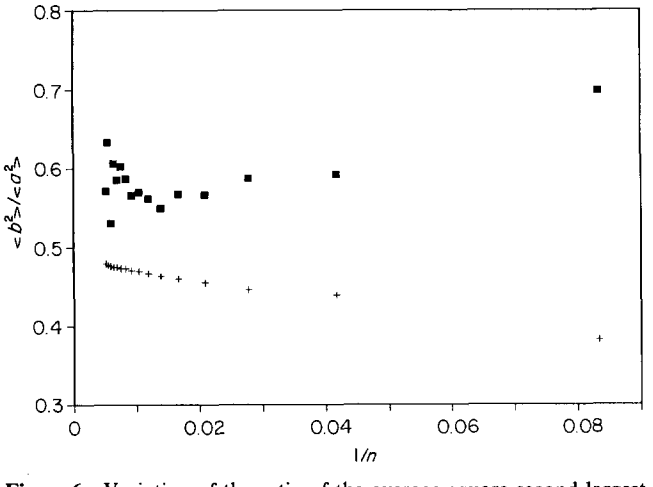

Figure 6 Variation of the ratio of the average square second largest to largest semi-axes for equivalent ellipsoids for ring (■) and chain (+) polyesters generated using the RISM

$12 \leqslant n \leqslant 192$ were calculated. *Figures 4*, *5* and *6*, respectively, show the variation of the ratios $\langle c^2\rangle/\langle a^2\rangle$, $\langle c^2\rangle/\langle b^2\rangle$ and $\langle b^2\rangle/\langle a^2\rangle$ with the reciprocal of the number of skeletal bonds ($1/n$). It can be seen that as n increases for the linear polyesters the ratios $\langle c^2\rangle/\langle a^2\rangle$, $\langle c^2\rangle/\langle b^2\rangle$ and $\langle b^2\rangle/\langle a^2\rangle$ increase; whereas for the cyclic polyester the ratio $\langle b^2\rangle/\langle a^2\rangle$ is found to decrease with increasing n. This implies that as the number of skeletal bonds increases the minimum energy conformations of the rings at 298 K become more circular in nature.

The ratio $\langle a^2\rangle:\langle b^2\rangle:\langle c^2\rangle$ for two cyclic and two linear polyesters (skeletal bonds $n = 120$ and 192) are compared with the limiting values ($n \to \infty$) for linear and cyclic PDMS[11] (*Table 3*). It can be seen that the values of $\langle a^2\rangle:\langle b^2\rangle:\langle c^2\rangle$ for the cyclic polyesters are considerably less than those of the linear polyesters, showing that the energy minimized conformations of the cyclic polyesters are more circular in nature. It is also apparent, from comparing the minimum energy conformations of PDMS and polyester rings, that the polyesters adopt a more circular structure (*Table 3*).

The numbers of polymer chains generated by the Monte Carlo method were similar to those in the study of the PDMS rings[12,13]. It is noted that because of the relatively small number of rings generated by the longer chain molecules, greater uncertainty is associated with the calculated values of their properties (*Figures 3–6*).

Molecular graphics

In addition to the Monte Carlo simulation for the study of the sizes and shapes of the cyclic polyester molecules, the energy minimized conformations at 0 K *in vacuo* were studied using molecular graphics. The molecular modelling was carried out using CHARMm molecular modelling computer software (Polygen Corporation) on a Silicon Graphics Personal IRIS workstation. The software is a molecular mechanics program that calculates the position and energies of a graphically generated molecular structure. The total energy of the system is expressed as a summation of internal energy components (i.e. bond potential, bond angle potential, dihedral angle potential and torsional potential) and non-bonded energy terms (i.e. Van der Waals interactions, electrostatic interactions, hydrogen bonding interactions, atom harmonics and dihedral constraints). The non-bonded interactions were calculated between all pairs of atoms according to specified cut-off distances.

Cyclic polyesters with the repeat unit $[(CH_2)_{10}$–CO.O] were graphically constructed using a computer software package called Quanta (Polygen Corporation). Using CHARMm the cyclic polyester was 'heated' at predefined intervals to 300 K, equilibrated at that temperature for a known time period (100 ps) and then finally 'cooled' to 0 K, during which time the total energy of the molecule system was calculated at intervals to determine the minimum energy conformation. The energy minimization technique was carried out using the Adopted Basis Newton

Table 3 Shape ratio parameters for some cyclic and linear polymers

Polymer	$\langle a^2\rangle$:	$\langle b^2\rangle$:	$\langle c^2\rangle$
Linear PDMS[a]	11.9	2.6	1
Cyclic PDMS[a]	5.9	2.6	1
Linear polyester (120 skeletal bonds)	4.2	2.0	1
Cyclic polyester (120 skeletal bonds)	2.8	1.7	1
Linear polyester (192 skeletal bonds)	4.1	2.0	1
Cyclic polyester (192 skeletal bonds)	3.0	1.7	1

[a] Limiting values[13]

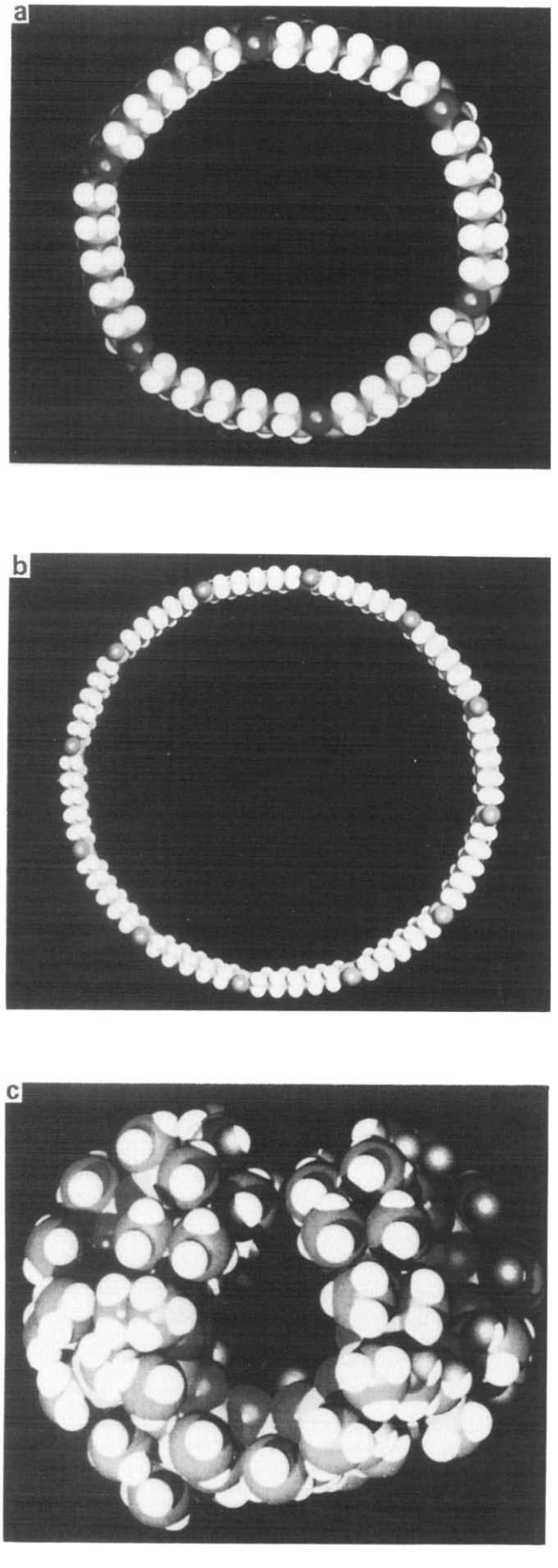

Figure 7 Energy minimized conformations obtained using CHARMm: (a) polyester ring, 72 skeletal bonds; (b) polyester ring, 144 skeletal bonds; (c) PDMS ring, 80 skeletal bonds

Raphson method. Polyester rings with skeletal bonds in the range $12 \leqslant n \leqslant 144$ were studied. Photographs are shown for the energy minimization conformations for two cyclic polyesters with 72 and 144 skeletal bonds (*Figures 7a* and *b*). For comparison purposes, the energy minimized conformations for cyclic PDMS were also studied. *Figure 7c* shows a representative cyclic PDMS molecule with 80 skeletal bonds. From the photographs for the minimized energy conformations for the cyclic polyesters and the cyclic PDMS it is apparent that the minimum energy conformations of the polyesters adopt more open structures, i.e. they are more circular in nature. This is in agreement with the observations for the 'shape' studies described earlier.

Despite the differences in the conformational properties of cyclic PDMS and cyclic polyesters, the rings are trapped to approximately equal extents in the PDMS networks (*Table 1*). The compatibility of PDMS and networks of its own kind may favour its entrapment. However, the ease with which cyclic polyesters form approximately circular conformations may assist in the trapping process. Further investigations of the preparation and properties of cyclic polyesters and related polymers are in progress.

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REFERENCES

1 Wood, B. R., Hodge, P. and Semlyen, J. A. *Polymer* 1993, **34**, 3052
2 Garrido, L., Mark, J. E., Clarson, S. J. and Semlyen, J. A. *Polym. Commun.* 1985, **26**, 53
3 Garrido, L., Mark, J. E., Clarson, S. J. and Semlyen, J. A. *Polym. Commun.* 1985, **26**, 55
4 Clarson, S. J., Mark, J. E. and Semlyen, J. A. *Polym. Commun.* 1986, **27**, 244
5 Clarson, S. J., Mark, J. E. and Semlyen, J. A. *Polym. Commun.* 1987, **28**, 151
6 Fyvie, T. J., Frisch, H. L., Semlyen, J. A., Clarson, S. J. and Mark, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1987, **9**, 2503
7 Huang, W., Frisch, H. L., Hua, Y. and Semlyen, J. A. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 1807
8 Dodgson, K., Sympson, D. and Semlyen, J. A. *Polymer* 1978, **19**, 1285
9 Flory, P. J. and Williams, A. D. *J. Polym. Sci. A2* 1967, **5**, 399
10 Jones, F. R., Scales, L. E. and Semlyen, J. A. *Polymer* 1974, **15**, 738
11 Knecht, M. R. and Elias, H. G. *Makromol. Chem.* 1972, **157**, 1
12 Edwards, C. J. C., Rigby, D., Stepto, R. F. T. and Semlyen, J. A. *Polymer* 1983, **24**, 395
13 Edwards, C. J. C., Rigby, D., Stepto, R. F. T., Dodgson, K. and Semlyen, J. A. *Polymer* 1983, **24**, 391
14 Winnik, M. A. *Chem. Rev.* 1981, **81**, 491
15 Sisido, M. *Macromolecules* 1971, **4**, 737
16 Semlyen, J. A. *Trans. Faraday. Soc.* 1967, **63**, 2342
17 Winnik, M. A., Trueman, R. E., Jackowski, G., Saunders, D. S. and Whittington, S. G. *J. Am. Chem. Soc.* 1974, **96**, 4843
18 Flory, P. J., Suter, U. W. and Mutter, M. *J. Am. Chem. Soc.* 1976, **98**, 5733
19 Suter, U. W., Mutter, M. and Flory, P. J. *J. Am. Chem. Soc.* 1976, **98**, 5740
20 Mutter, M., Suter, U. W. and Flory, P. J. *J. Am. Chem. Soc.* 1976, **98**, 5745