ELSEVIER

Polymer 41 (2000) 1487–1495

polymer

Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 16. Theoretical and experimental investigations of cyclics prepared from poly(decamethylene fumarate) and poly(decamethylene maleate) ring-chain equilibrium reactions[☆]

R.E. Heath, B.R. Wood, J.A. Semlyen*

Department of Chemistry, University of York, York, YO10 5DD, UK

Received 1 January 1999; received in revised form 20 March 1999; accepted 29 March 1999

Abstract

The molar cyclisation equilibrium constants K_x for cyclics $[OCOCH{=}CHCOO(CH_2)_{10}]_x$ (with $x = 1$–7) in two closely related polyester systems, poly(decamethylene maleate) and poly(decamethylene fumarate), were measured experimentally using gel permeation chromatography. The corresponding theoretical K_x values were calculated by two methods. The first applied a rotational isomeric state model to describe the statistical conformations of chains forming rings and it assumed that such chains obey Gaussian statistics. The second approach used MSI's program Insight II to perform the Monte Carlo Metropolis calculations. When the expected chain expansion effects in a good solvent media was considered, a good agreement between experiment and theory for all the cyclics with $x \geq 2$ was found. Crown copyright © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Cyclics; Ring-chain equilibrium; Poly(decamethylene maleate)

1. Introduction

In the first fifteen papers in this series [1–15], experimental equilibrium cyclic concentrations in polymeric systems were compared with the theoretical values calculated using the Jacobson and Stockmayer theory [16,17], by using rotational isomeric state models to describe the statistical conformations of the corresponding open chain molecules. In recent years, there have been important developments in both experimental techniques for determining cyclic concentrations and in theoretical and computational methods. These aspects, coupled with the success of the previous correlations between experiment and theory, have encouraged us to explore the method for two closely related polyesters, poly(decamethylene maleate) (PDM) and poly(decamethylene fumarate) (PDF). The structures of these polyesters differ only in the *cis* and *trans* configurations about the alkene linkage.

Two methods for calculating the equilibrium cyclic concentrations in the PDM and PDF systems have been applied. These involve (i) the use of established rotational isomeric state models [18,19] coupled with application of the matrix algebraic methods of Flory and Jernigan [20,21], and (ii) the calculation of intramolecular cyclisation probabilities using Monte-Carlo Metropolis (MCM) methods. The first method assumes that the Gaussian statistics apply and the validity of this assumption was investigated by the second method.

This work is part of a general exploration of the preparation, fractionation, characterisation and investigation of large ring esters and ether–esters [22–30]. Such materials may find applications as plasticisers, complexing agents [31,32] and even conducting polymers [33]. Ring-chain equilibrium reaction conditions were established for the PDM and PDF systems, allowing for the measurement of equilibrium cyclic concentrations. The results of this experimental and theoretical study are presented in this paper.

2. Experimental

2.1. Materials

Dimethyl fumarate, dimethyl maleate, and the two catalysts dibutyltin bis(2-ethyl hexanoate) and titanium (IV)

---

* Corresponding author.

[☆] Published with the permission of the Controller of Her Majesty's Stationary Office.

PII: S0032-3861(99)00262-1

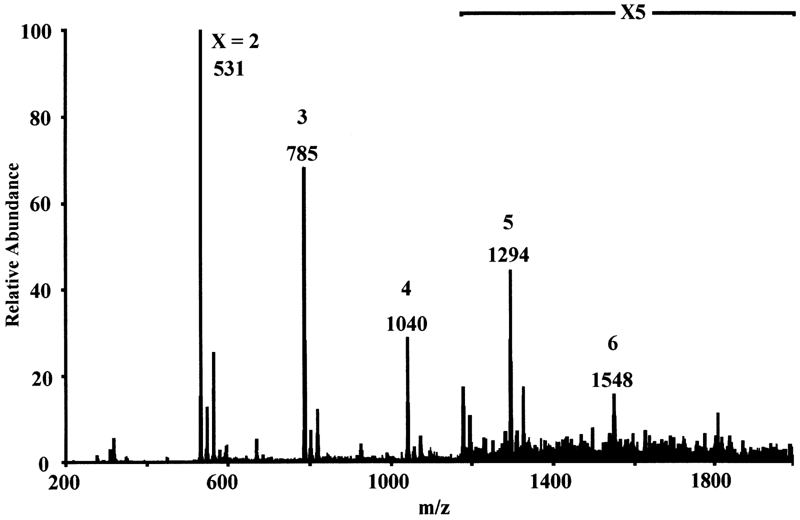

Fig. 1. ESI-MS of the PDM ring-chain equilibrium products showing the presence of *x*-meric cyclics.

isopropoxide were obtained from Aldrich Chemical Co. 1,10-decandiol was obtained from Lancaster Synthesis Ltd. All of the materials were used as obtained.

2.2. Preparation of linear polyesters

Equimolar portions of 1,10-decandiol and dimethyl maleate or fumarate were heated to 100°C, to ensure complete melting and mixing of the reagents, under dry nitrogen in a three necked flask equipped with a distillation head. The catalyst, titanium (IV) isopropoxide (0.5 wt.%), was then added and the temperature raised to 150°C for 24 h, during which methanol distilled off. The temperature was then decreased to 120°C and the system placed under vacuum (water pump) to remove further methanol. After a further 24 h, the linear polymer produced was allowed to cool to room temperature under dry nitrogen. The PDM and PDF polymers were found to have a number-average molar mass of 5000 g mol^{-1}, quite low but sufficient for ring chain equilibria to be set up.

2.3. Preparation of cyclic esters

Linear PDF or PDM previously prepared was diluted in chlorobenzene at 50/1 (vol. chlorobenzene/wt. polymer) with 1 wt.% dibutyltin bis(2-ethylhexanote), the transesterification catalyst. The solution was heated to reflux (130°C) and the samples were taken and analysed by gel permeation chromatography (GPC) at regular intervals to study the progress of reaction, observing the decrease in the amount

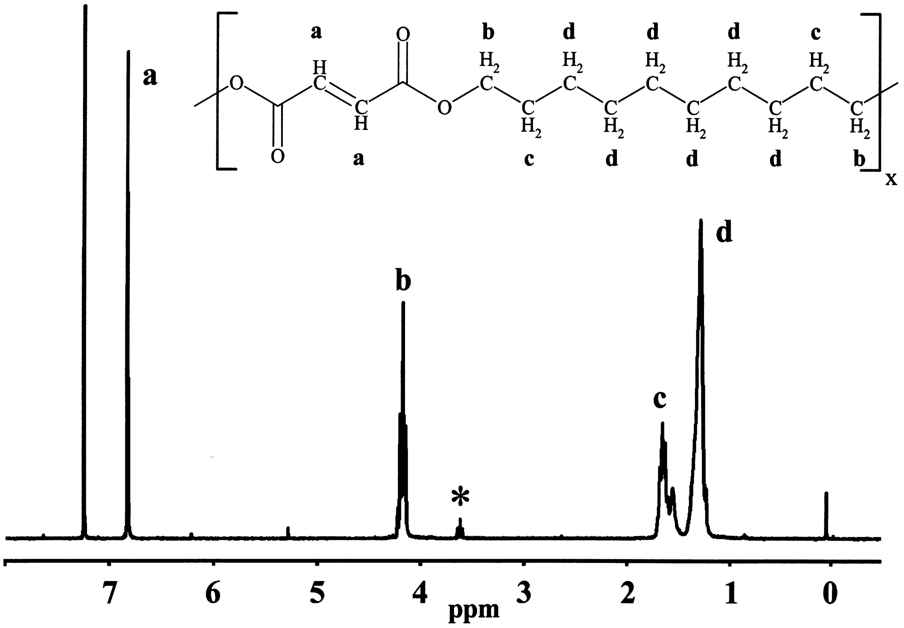

Fig. 2. ^{1}H NMR spectra of PDF ring-chain equilibrium products showing the presence of end groups (marked $*$).

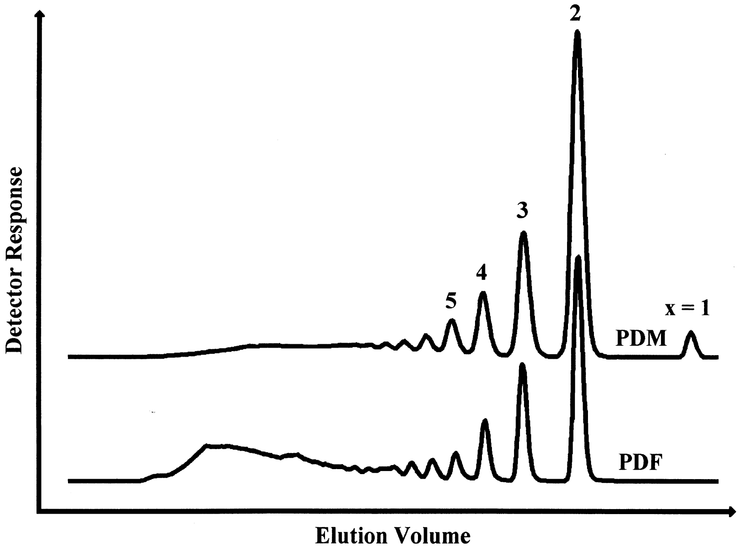

Fig. 3. Gel permeation chromatograms of PDM and PDF ring-chain equilibria products showing the presence of *x*-meric cyclic species.

of chains present and the corresponding increase in the quantity of cyclics. When equilibrium was reached, the solution was cooled to room temperature and the solvent removed.

2.4. Analytical techniques

GPC analysis of the linear and cyclic polyesters was performed using a Knauer GPC instrument, equipped with four PL-gel 3 μm mixed-E columns, supplied by Polymer Laboratories Ltd. The detector used was a Polymer Laboratories evaporative mass detector (PL-EMD 960). Chloroform was used as the chromatographic solvent at a flow rate of 0.3 ml min^{-1}.

Nuclear magnetic resonance studies (NMR) studies were performed on an Joel 270 MHz spectrometer with deuterated chloroform as the solvent. Mass spectroscopy was performed using electrospray ionisation (ESI) on an Finnigan-MAT LCQ instrument.

3. Results

The products of the ring-chain equilibrium reactions were characterised using GPC, NMR and ESI-MS. Mass spectroscopy showed molecular ions corresponding to the correct molar masses for the expected cyclic species (Fig. 1). NMR showed that the end groups were present in the products of all the ring-chain equilibria (Fig. 2) as would be expected.

GPC analysis of the ring-chain equilibrium products gave yields of cyclics for the PDM and PDF systems as 78 and 50 wt.%, respectively (Fig. 3). There was no detectable quantity of the monomer ring formed in the PDF system, and in the PDM system the monomeric cycle was formed in a much lower concentration than the dimer (Table 1).

The equilibrium ring-chain reactions established may be described as

$$\text{–M}_y\text{–} \rightleftharpoons \text{–M}_{y-x}\text{–} + \text{M}_x \tag{1}$$

where M is the monomer unit, M_x represents *x*-meric cyclic species, and $\text{–M}_y\text{–}$ and $\text{–M}_{y-x}\text{–}$ are linear species with *y* and $y-x$ monomer units, respectively. The molar cyclisation equilibrium constant K_x for an *x*-meric cyclic is given by

$$K_x = \frac{[\text{–M}_{y-x}\text{–}][\text{M}_x]}{[\text{–M}_y\text{–}]} \tag{2}$$

The value of K_x can be calculated knowing the concentrations of the individual rings $[\text{M}_x]$ and the extent of reaction of functional groups in the chain *p* using the relationship [34]

$$K_x = \frac{[\text{M}_x]}{p^x} \tag{3}$$

where

$$p = 1 - \frac{M_0}{\bar{M}_\text{n}} \tag{4}$$

where M_0 is the molar mass of the repeat unit, and $\bar{M}_\text{n}$ is the number average molar mass for the linear molecules present.

The evaporative mass detector used has a response that is proportional to the mass of sample eluted, hence the mass of each of the rings can be calculated by integrating the peak areas on the GPC traces using the Logical GPC software. This provides greater accuracy in determining the cyclic concentrations than some other types of detector (e.g. refractive index), where it must be assumed that all the various cyclic species respond proportionally to their molar masses. This mass information, combined with the known molar masses for the different cyclic species, enables the cyclic concentrations (and hence the K_x values) of the cyclics M_x (in this case $1 < x < 7$) to be accurately

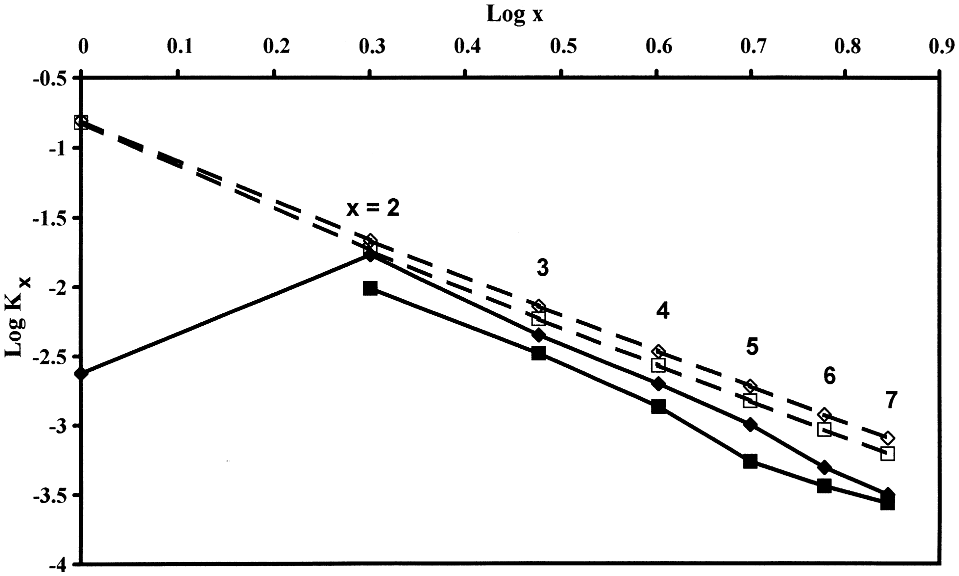

Fig. 4. Molar cyclisation equilibrium constants plotted as log K_x against log x for the PDM (–◆–) and PDF (–■–) systems compared to the predicted values from the RIS method (PDM (- -◇- -) and PDF (- -□- -)).

determined. A plot of log K_x against log x for the PDM and PDF systems is shown in Fig. 4.

4. Theoretical determination of molar cyclisation equilibrium constants

Molar cyclisation equilibrium constants may be calculated using the Jacobson–Stockmayer theory [16,17], which states that

$$K_x = \frac{W_x(\underline{0})}{N_A \sigma_{R_x}}, \tag{5}$$

where N_A is Avogadro's number, $W_x(\underline{0})$ is the density of end-to-end vectors in the region $\underline{r} \cong \underline{0}$, and σ_{R_x} is the symmetry number of an x-meric ring, which in this case is $2x$, where x is the number of repeat units.

The distribution $W_x(\underline{r})$ (and hence the value of $W_x(\underline{0})$) may be calculated directly by the MCM simulation of the polymer chain or calculated from values of $\langle r_x^2 \rangle$ assuming the chain obeys Gaussian statistics. For a Gaussian distribution

$$W_x(\underline{r}) = \left(\frac{3}{2\pi\langle r_x^2\rangle}\right)^{3/2} \exp\left(-\left(\frac{3}{2\langle r_x^2\rangle}\right) r^2\right). \tag{6}$$

When the end-to-end vector is of length $\underline{0}$, this simplifies to

$$W_x(\underline{0}) = \left(\frac{3}{2\pi\langle r_x^2\rangle}\right)^{3/2}. \tag{7}$$

The assumption that the chain obeys Gaussian statistics will only hold when the chains are of sufficient length and flexibility, and this aspect is examined later in this paper.

4.1. The rotational isomeric state model

The rotational isomeric state (RIS) model, developed and applied by Flory, his co-workers and others [18,35], was used to calculate the values of $\langle r_x^2 \rangle_0$ (with the subscript 0 denoting values which are unperturbed by excluded volume effects) for the PDF and PDM chains with $1 < x < 7$. The model assumes that each skeletal bond in a polymer chain may be assigned to one of a discrete number of RIS's (e.g. for a C–C bond in polyethylene, the states are *trans*

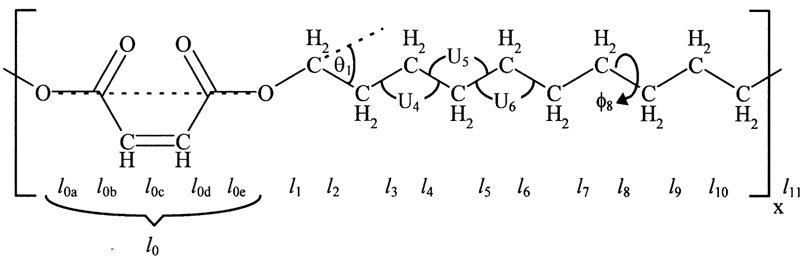

Fig. 5. The assigned chain parameters for the PDM repeat unit.

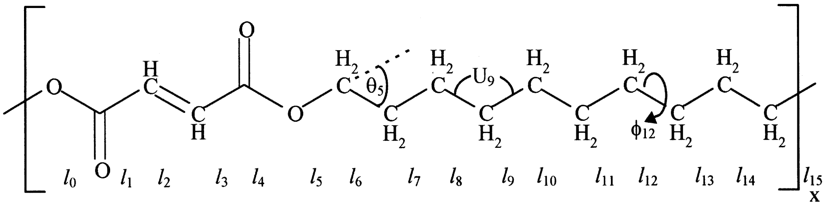

Fig. 6. The assigned chain parameters for the PDF repeat unit.

($t, \phi = 0°$), *gauche* + ($g^{+}, \phi = 120°$) and *gauche* − ($g^{-}, \phi = 240°$) [36]). The chains described here are assigned structural parameters, which have mostly been defined earlier by Flory and Williams [18], and were applied by Jones and Scales [13] (Figs. 5 and 6).

The bond lengths l_i used were: CH_2–CH_2 = 1.53 Å, CH_2–O = 1.44 Å, CO–O = 1.33 Å, CO–CH = 1.49 Å, and CH = CH = 1.34 Å [37]. The bond angle supplements, θ_i, used were: CH_2–CH_2–CH_2 = 68°, O–CH_2–CH_2 = 70°, CO–O–CH_2 = 67°, CH–CO–O = 69.5° and CH=CH–CO = 60° [37].

In PDM there are restricted rotations in the ester and the alkene groups (bonds 0a and 0e being always *trans* and bond 0c being *cis*). Calculations using HyperChem [38] have predicted bonds 0b and 0d to exist almost exclusively in the *trans* state. Due to these restricted rotations, bonds 0a, 0b, 0c, 0d and 0e may be simplified to a single bond 0 spanning their range (Fig. 5). The statistical weight matrices U_i for the PDM chain at 423 K are [13,18]

$$U_0 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{8}$$

$$U_1 = \begin{bmatrix} 1 & 1 & 1 \end{bmatrix} \tag{9}$$

$$U_2 = U_{10} = U_{11} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0.2 \\ 1 & 0.2 & 1 \end{bmatrix} \tag{10}$$

$$U_3 = \begin{bmatrix} 1 & 0.55 & 0.55 \\ 1 & 0.55 & 0.11 \\ 1 & 0.11 & 0.55 \end{bmatrix} \tag{11}$$

$$U_4 = U_5 = U_6 = U_7 = U_8 = U_9 = \begin{bmatrix} 1 & 0.55 & 0.55 \\ 1 & 0.55 & 0.05 \\ 1 & 0.05 & 0.55 \end{bmatrix} \tag{12}$$

The elements of the matrices are the statistical weights, u, calculated using the following equation

$$u = \exp^{-\Delta E/RT}, \tag{13}$$

where ΔE is the difference in energy for a defined set of interactions when bonds $i-1$ and i are in discrete RISs (based on the position of u in the statistical weight matrix), relative to the *trans–trans* state. The interactions considered here are those between atoms and groups separated by only three or four skeletal bonds, with each interaction included in one of the statistical weight matrices below [18,19]. T is the temperature and R is the gas constant.

For PDM, the elements in the rows and columns of the matrices correspond to $\phi = 0$, 120 and 240° except in U_0 and U_1 where the column and row, respectively, correspond to $\phi = 180°$.

In PDF, bonds 2 and 4 (which correspond to 0b and 0d in PDM) can exist in either a *cis* or *trans* form, hence a virtual bond of the type seen in PDM is not present. The two states were estimated to have equal weighting by consideration of the relevant interactions using HyperChem [38]. The statistical weight matrices for the PDF chain at 423 K are [13,18]

$$U_0 = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{14}$$

$$U_1 = U_3 = \begin{bmatrix} 1 & 1 \end{bmatrix} \tag{15}$$

$$U_2 = U_4 = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{16}$$

$$U_5 = \begin{bmatrix} 1 & 1 & 1 \end{bmatrix} \tag{17}$$

$$U_6 = U_{14} = U_{15} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0.2 \\ 1 & 0.2 & 1 \end{bmatrix} \tag{18}$$

$$U_7 = \begin{bmatrix} 1 & 0.55 & 0.55 \\ 1 & 0.55 & 0.11 \\ 1 & 0.11 & 0.55 \end{bmatrix} \tag{19}$$

$$U_8 = U_9 = U_{10} = U_{11} = U_{12} = U_{13} = \begin{bmatrix} 1 & 0.55 & 0.55 \\ 1 & 0.55 & 0.05 \\ 1 & 0.05 & 0.55 \end{bmatrix} \tag{20}$$

For PDF, the elements in the rows and columns of the matrices correspond to $\phi = 0$, 120 and 240° with some exceptions. In U_0 and U_5, the column and row, respectively, correspond to $\phi = 0°$. In U_1–U_4, the column or row with one element corresponds to $\phi = 0°$, and the column or row with two elements correspond to $\phi = 0$ and 180°.

The first and last repeat units in the chain require careful consideration. The first statistical weight matrix (U_0) for the first repeat unit in a chain requires replacing with the identity matrix E_3. The final repeat unit has a bond less than the other repeat units. Therefore, the last statistical weight matrix (U_{11} for PDM and U_{15} for PDF) (and hence G_{11} or G_{15}) is dropped and the penultimate statistical weight matrix (U_{10} or U_{14}) is replaced by the same size identity matrix E_3.

The value of $\langle r_x^2 \rangle_0$ can be calculated as follows [18]

$$\langle r_x^2 \rangle_0 = 2Z^{-1} J^* G_1^{(\xi_1)} G^{(\xi)^{x-2}} G_x^{(\xi_x)} J \tag{21}$$

with J^* and J defined as the row and column

$$J^* = \begin{bmatrix} 1 & 0 & \cdots & 0 & 0 \end{bmatrix} \tag{22}$$

$$J = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 1 \\ 1 \end{bmatrix} \tag{23}$$

consisting of the correct number of elements relative to $G^{(\xi)}$, in this case 15.

The conformational partition function Z is defined as

$$Z = \mathrm{J}^* U_1^{(\xi_1)} U^{(\xi)^{x-2}} U_x^{(\xi_x)} \mathrm{J}, \tag{24}$$

where $U^{(\xi)}$ is the product of the statistical weight matrices for a ξ bond repeat unit

$$U^{(\xi)} = U_1 \quad U_2 \quad \cdots \quad U_\xi \tag{25}$$

and J^* and J are the row and column

$$\mathrm{J}^* = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \quad \text{and} \quad \mathrm{J} = \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \tag{26}$$

$U_1^{(\xi_1)}$ and $U_x^{(\xi_x)}$ are calculated in the same way as $U^{(\xi)}$ (Eq. (25)) for the ξ_1 bond first repeat unit and the ξ_x bond final repeat unit, respectively.

In a similar fashion to $U^{(\xi)}$, $G^{(\xi)}$ is the product of the G matrices for a ξ bond repeat unit

$$G^{(\xi)} = G_1 \quad G_2 \quad \cdots \quad G_\xi \tag{27}$$

where for the ith bond of the repeat unit, the 15×15 generator matrix G_i is given by

$$G_i = \begin{bmatrix} U_i & (U_i \otimes l_i^{\mathrm{T}})\|T_i\| & (l_i^2/2)U_i \\ 0 & (U_i \otimes E_3)\|T_i\| & U_i \otimes \mathrm{l}_i \\ 0 & 0 & U_i \end{bmatrix} \tag{28}$$

where the bond vector, l_i, is defined as

$$\mathrm{l}_i = \begin{bmatrix} l_i \\ 0 \\ 0 \end{bmatrix} \tag{29}$$

and $\|T_i\|$ is the pseudo diagonal matrix for converting bond $i + 1$ into the same coordinate system as bond i

$$\|T_i\| = \begin{bmatrix} T_0 & 0 & 0 \\ 0 & T_{120} & 0 \\ 0 & 0 & T_{240} \end{bmatrix} \tag{30}$$

with elements

$$T_\phi = \begin{bmatrix} \cos\theta_i & \sin\theta_i & 0 \\ \sin\theta_i \cos\phi & -\cos\theta_i \cos\phi & \sin\phi \\ \sin\theta_i \sin\phi & -\cos\theta_i \sin\phi & -\cos\phi \end{bmatrix}. \tag{31}$$

The values of $\langle r_x^2 \rangle_0$ generated in this way were used to calculate $W_x(\underline{0})$ values with Eq. (7), and from these K_x values were obtained (Fig. 4). The characteristic ratios for the two polymers, C_x, were also calculated from $\langle r_x^2 \rangle_0$ values using Eq. (32).

$$C_x = \frac{\langle r_x^2 \rangle_0}{nl^2}, \tag{32}$$

where n is the number of skeletal bonds in the chain and l^2 is the mean-square bond length. Values of C_∞ were predicted from the values of C_x for large values of x, and were found to be 5.7 and 6.9 for the PDM and PDF systems, respectively.

In the program, all of the matrices in Eqs. (8)–(30) were checked by hand to ensure they had the correct form. The end-to-end distance, r, and the statistical weight of each of the 19683 PDM monomer chain conformations were calculated and the value of $\langle r_x^2 \rangle_0$ found to match that of the matrix method outlined above.

4.2. Monte-Carlo metropolis simulation

The second method used to calculate $W_x(\underline{0})$ was a MCM approach using MSI's program Insight II [39]. This method is similar to the RIS method in that it assumes that the bond rotations are of far greater significance than the bond stretching, bond distortion, etc. and hence, the latter effects can be ignored. Unlike the RIS method though, the MCM method does not restrict bond rotation to three discrete states, it allows full rotation of bonds through 360°. In agreement with previous treatments, only short-range interactions within the chains are taken into account in the form of first

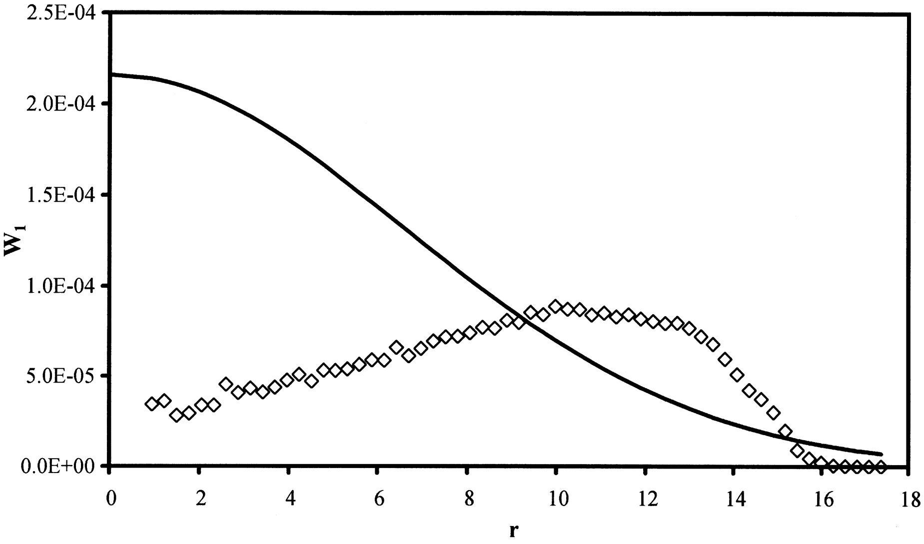

Fig. 7. Probability density distribution $W_1(\underline{r})$ for the PDM monomer calculated by the MCM method (◇) compared to the distribution calculated from $\langle r_1^2 \rangle_0$, assuming that Gaussian statistics apply (—).

and second order (three and four bond) interactions. Instead of using the statistical weight matrices to calculate the probabilities of different conformations, the MCM method uses a force field approach. The force field used here is the PCFF force field, the polymer extension of the CFF force field, which was parameterised for aromatic esters by Sun [40]. It has not been fully parameterised for the systems investigated here with some torsions adopting the default parameters, which appeared reasonable. The appropriate linear molecule was subjected to 100 000 MCM equilibrium steps, and then 500 000 steps were used to generate $W_x(\underline{r})$ (Figs. 7 and 8) and $\langle r_x^2 \rangle_0$ at 405 K. The results show that the longer chains more closely fit the Gaussian assumption, with $W_x(\underline{r})$ for the 15 bond PDM monomer chain (Fig. 7) showing significant variation from the expected Gaussian distribution.

$W_x(\underline{0})$ was calculated in two ways from the data obtained. The first method used the value of $W_x(\underline{0})$ directly from the distribution $W_x(\underline{r})$, and the second used the value of $\langle r_x^2 \rangle_0$ generated from the simulation with Eq. (7), assuming a Gaussian distribution of end-to-end vectors (Figs. 9 and 10). The MCM model predicts cyclic concentrations that are greater than that observed experimentally (especially for the monomer) (Table 1), but the trends in the experimental results are clearly reproduced by the model. The values of C_∞ for PDM and PDF, calculated from C_x values, are 6.3 and 7.6, respectively, which compare well with the values calculated from the RIS method (5.7 and 6.9). The

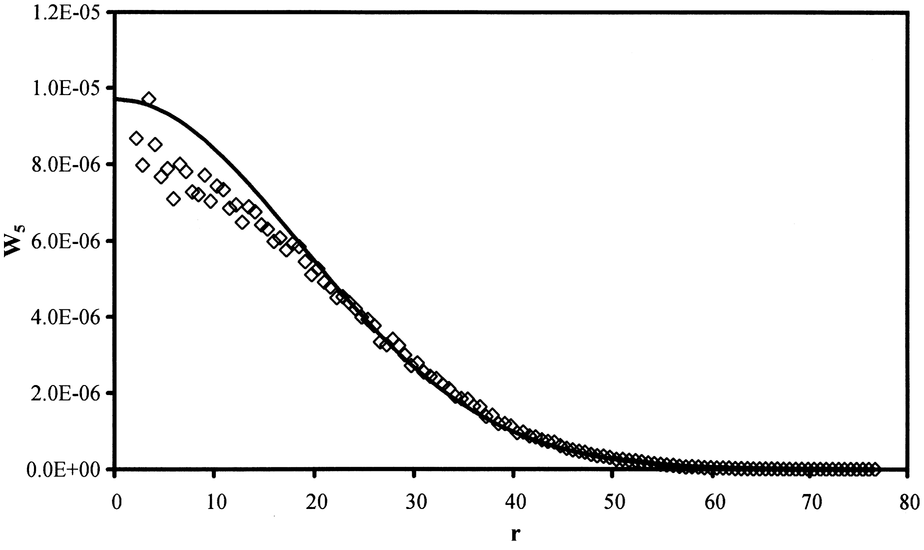

Fig. 8. Probability density distribution $W_5(\underline{r})$ for the PDM pentamer calculated by the MCM method (◇) compared to the distribution calculated from $\langle r_5^2 \rangle_0$, assuming that Gaussian statistics apply (—).

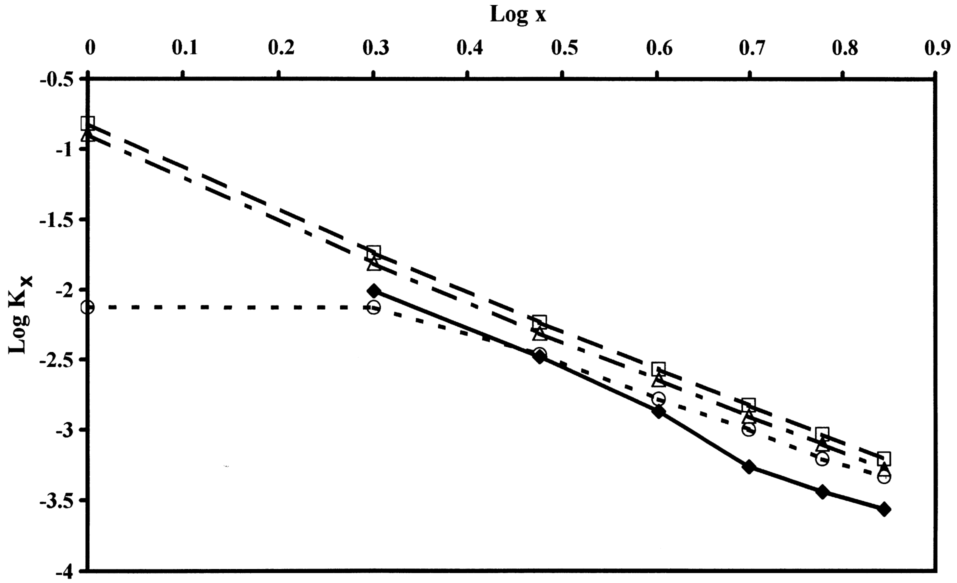

Fig. 9. Molar cyclisation equilibrium constants plotted as log K_x against log x for the PDF system (–◆–), compared to the calculated values by the RIS method (- -□- -) and the MCM method (using $\langle r_x^2 \rangle_0$ values assuming Gaussian statistics (- -△- -) and the distribution $W_x(\underline{r})$ (- -○- -) to find $W_x(\underline{0})$).

effect of variation of the dielectric constant from 1 to 4.3 (the dielectric constant for chlorobenzene at 405 K) was found to be very small, with all values within the errors of the calculation. All other calculations were performed with the dielectric constant set to 1.

5. Concluding remarks

The RIS method and the MCM method correlate well for all but the shortest chains (Figs. 9 and 10) showing that the statistical weights used in the RIS method compare favourably to the interactions generated by the force field. The differences in the experimental K_x values for the PDF and PDM systems are predicted accurately by the models, but the actual values of K_x are calculated to be higher than found experimentally for $x > 2$ (Fig. 4). This difference may arise from the excluded volume effects resulting in chain expansion, and hence lower cyclic concentrations in chlorobenzene, which is not a theta solvent [34] for these polymers so $\langle r_x^2 \rangle$ would be expected to be larger than $\langle r_x^2 \rangle_0$.

The MCM method shows the calculated values of $W_x(\underline{r})$ for the monomers ($x = 1$) to differ significantly from Gaussian distributions (Fig. 7), giving low values of $W_x(\underline{0})$ in

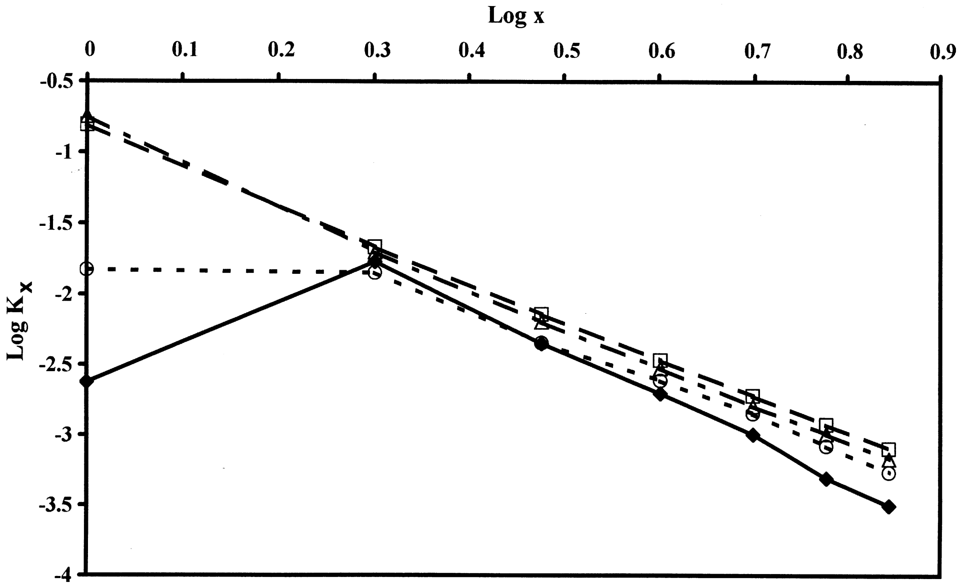

Fig. 10. Molar cyclisation equilibrium constants plotted as log K_x against log x for the PDM system (–◆–) compared to the calculated values by the RIS (- -□- -) and the MCM method (using $\langle r_x^2 \rangle_0$ values assuming Gaussian statistics (- -△- -) and the distribution $W_x(\underline{r})$ (- -○- -) to find $W_x(\underline{0})$).

Table 1
Comparison of the experimental cyclic concentrations with those calculated by the MCM model for PDM and PDF

Number of repeat units x	Wt.% cyclics			
	PDM		PDF	
	Experimental	MCM	Experimental	MCM
1	2.9	18.3	0.0	9.3
2	40.3	33.7	23.9	18.3
3	15.4	15.5	11.9	12.4
4	8.8	10.8	6.4	7.8
5	5.4	7.6	3.2	5.8
6	3.0	5.2	2.5	4.3
7	2.2	3.8	2.1	3.6
Total	78.0	94.9	50.0	61.5

agreement with the low concentrations of these cyclics observed experimentally. This shows that the Gaussian statistics do not apply for these short chain molecules, and hence the RIS method is inaccurate for these chains as it relies on a Gaussian distribution of $W_x(\underline{r})$ (as does the MCM method when $W_x(\underline{0})$ is calculated from $\langle r_x^2 \rangle_0$). The MCM method also shows that as the chain length increases, $W_x(\underline{r})$ becomes more Gaussian (see Fig. 8 for the 79 skeletal bond PDM pentamer chain), and hence the RIS method should become more accurate.

In summary, the RIS and MCM methods can be used to predict the molar cyclisation equilibrium constants in the PDM and PDF systems for cyclics with 32–112 bonds. This study provides a bridge between small organic molecules and polymeric molecules, and has demonstrated a good match between experimental and theoretical data for molar cyclisation equilibrium constants in the two systems investigated in this paper.

Acknowledgements

We thank the Defence Evaluation Research Agency and the University of York for providing financial support for R.E. Heath. We also thank the York Structural Biology Centre for the use of their computing facilities and Prof. R.F.T. Stepto and Dr D.J.R. Taylor of the Manchester Materials Centre for helpful discussions. The NMR and MS services of the University of York are also gratefully acknowledged.

References

[1] Semlyen JA, Wright PV. Polymer 1969;10:543.
[2] Semlyen JA, Walker GR. Polymer 1969;10:597.
[3] Wright PV, Semlyen JA. Polymer 1970;11:462.
[4] Walker GR, Semlyen JA. Polymer 1970;11:472.
[5] Beevers MS, Semlyen JA. Polymer 1971;12:373.
[6] Semlyen JA. Polymer 1971;12:383.
[7] Andrews JM, Semlyen JA. Polymer 1972;13:142.
[8] Beevers MS, Semlyen JA. Polymer 1972;13:385.
[9] Cooper DR, Semlyen JA. Polymer 1972;13:414.
[10] Beevers MS, Semlyen JA. Polymer 1972;13:523.
[11] Cooper DR, Semlyen JA. Polymer 1973;14:185.
[12] Andrews JM, Jones FR, Semlyen JA. Polymer 1974;15:420.
[13] Jones FR, Scales LE, Semlyen JA. Polymer 1974;15:738.
[14] Scales LE, Semlyen JA. Polymer 1976;17:601.
[15] Dodgson K, Heath RE, Semlyen JA. Polymer 1999;40:3995.
[16] Jacobson H, Stockmayer WH. J Chem Phys 1950;18:1600.
[17] Jacobson H, Beckmann CO, Stockmayer WH. J Chem Phys 1950;18:1607.
[18] Flory PJ. Statistical Mechanics of Chain Molecules. New York: Interscience, 1969.
[19] Mattice WL, Suter UW. Conformational Theory of Large Molecules. New York: Wiley, 1994.
[20] Flory PJ. Proc Natl Acad Sci USA 1964;51:1060.
[21] Flory PJ, Jernigan RL. J Chem Phys 1965;42:3059.
[22] Wood BR, Hodge P, Semlyen JA. Polymer 1993;34:1542.
[23] Wood BR, Joyce SJ, Scrivens G, Semlyen JA, Hodge P, O'Dell R. Polymer 1993;34:3059.
[24] Wood BR, Semlyen JA, Hodge P. Polymer 1994;35:1542.
[25] Wood BR, Semlyen JA, Hodge P. Polymer 1997;38:191.
[26] Hamilton SC, Semlyen JA. Polymer 1997;38:1685.
[27] Bryant JJL, Semlyen JA. Polymer 1997;38:2475.
[28] Bryant JJL, Semlyen JA. Polymer 1997;38:4531.
[29] Hamilton SC, Semlyen JA, Haddleton DM. Polymer 1998;39:3241.
[30] Wood BR, Hamilton SC, Semlyen JA. Polymer International 1997;44:397.
[31] Gokel GW. In: Semlyen JA, editor. Larger Ring Molecules. Chichester: Wiley, 1996.
[32] Gokel GW. Crown Ethers and Cryptands. Cambridge: Royal Society of Chemistry, 1991.
[33] Bruce PG, Vincent CA. J Chem Soc Faraday Trans 1993;89:3187.
[34] Flory PJ. Principles of Polymer Chemistry. Ithaca, NY: Cornell University Press, 1953.
[35] Volkenstein M. Configurational Statistics of Polymeric Chains. New York: Interscience, 1963.
[36] Sisido M. Macromolecules 1971;4:737.
[37] Lide DR, editor. CRC Handbook of Chemistry and Physics, 76th edn. Boca Raton: CRC Press, 1995.
[38] HyperChem, Version 5.1, Hypercube Inc., Gainesville, FL.
[39] Insight II, Version 4.0.0, Molecular Simulations Inc., San Diego, CA.
[40] Sun H. J Comput Chem 1994;15:752.