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## Macrocyclization of Poly(thiaethylene)

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**Abstract:** Cyclization of an acyclic poly(thiaethylene) chain to form  $(\text{CH}_2\text{CH}_2\text{S})_x$  has been studied by Monte Carlo methods for even  $x$  ranging from 4 to 24. Unperturbed acyclic chains are assumed to behave in accord with a rotational isomeric state treatment which incorporates first- and second-order interactions. The most readily formed macrocycle is that with  $x = 6$ , in harmony with results obtained in the poly(oxyethylene) series. However, cyclization at all  $x$  considered is found to be more difficult for poly(thiaethylene) than for the equivalent poly(oxyethylene). The greater difficulty in cyclization of poly(thiaethylene) can be attributed to the increase in C-X bond length and decrease in C-X-C angle when X is changed from an oxygen to a sulfur atom. Large macrocycles in both series have similar asymmetries, as measured by ratios of averaged principal moments of the inertia tensors.

Cyclic poly(oxyethylenes),  $(\text{CH}_2\text{CH}_2\text{O})_x$ , are of great interest because certain members of this series form strong, selective complexes with cations.<sup>1-5</sup> As a consequence, cyclic poly(oxyethylenes) have been promoted as models for biological cation transport and for use in fractionation of cations. Stable complexes with cations are also formed by certain cyclic poly(thiaethylenes),  $(\text{CH}_2\text{CH}_2\text{S})_x$ .<sup>6,7</sup> Members of this series form complexes which exhibit optical and redox properties reminiscent of those observed with blue copper proteins.<sup>6</sup>

Considerable effort has been expended in development of synthetic procedures which produce high yields of these macrocycles. In most cases the final step is an intramolecular reaction of  $\text{Y}(\text{CH}_2\text{CH}_2\text{X})_{x-1}\text{CH}_2\text{CH}_2\text{X}^-$ , where X is an oxygen or sulfur atom and Y is a suitable leaving group.<sup>1,2,8,9</sup> Yields in the oxygen series go through a maximum when  $x$  is 6. A yield as high as 93% has been reported for preparation of  $(\text{CH}_2\text{CH}_2\text{O})_6$ .<sup>8</sup> Occurrence of a maximum at  $x = 6$  is in harmony with the properties of unperturbed acyclic poly(oxyethylenes). Simultaneous occurrence of a zero end-to-end distance and proper angular correlation of terminal bonds is more probable when  $x$  is 6 than for any other even  $x$  in the range 4-20.<sup>10</sup> A template effect arising from the presence of potassium ions in the reaction mixture may also contribute to the high yield for  $(\text{CH}_2\text{CH}_2\text{O})_6$ . Cyclization tends to become more difficult when oxygen atoms are replaced by sulfur atoms. Macrocycles for which  $x$  is 6 illustrate this point. While yields for the oxygen-containing macrocycle are reported to be as high as 93%, those for the sulfur-containing macrocycle are only 25-35%.<sup>9</sup> Lower yields in the sulfur-containing series are also observed when the macrocycle formed contains an aromatic ring.<sup>11-13</sup>

One objective here is to assess whether the reduced tendency for cyclization seen with the sulfur-containing polymers might arise from a decrease in the probability for a zero end-to-end

distance in the unperturbed acyclic chain. A second goal is to determine how substitution of sulfur for oxygen atoms alters average configuration-dependent properties for macrocycles actually formed. These objectives are met by first constructing a rotational isomeric state model for poly(thiaethylene). This model is similar to one recently described in preliminary form by Abe.<sup>14</sup> Subsequent development is based on an adaptation of Flory's macrocyclization theory<sup>15</sup> used previously to investigate cyclization of poly(oxyethylene).<sup>10,16</sup>

### Conformational Energies

**Geometry.** Lengths of 1.10, 1.53, and 1.82 Å were used for C-H, C-C, and C-S bonds, respectively. The first two values are those appropriate for poly(methylene)<sup>17</sup> and poly(oxyethylene),<sup>18</sup> while that for the C-S bond is the one found in cysteine.<sup>19</sup> A length 0.005 Å shorter has been used for the C-S bond in poly(thiaethylene).<sup>14</sup> The C-S-C and C-C-S angles were 102 and 114°, respectively.<sup>14</sup>

**Conformational Energy Calculations.** Conformational energy was calculated as the sum of 6-12 potentials and intrinsic torsional potentials. Parameters for 6-12 potentials were formulated in the manner described by Brant et al.<sup>20</sup> Polarizabilities, effective number of electrons, and van der Waals radii were the following: carbon atom, 0.93 Å<sup>3</sup>, 5, 1.70 Å; hydrogen atom, 0.42 Å<sup>3</sup>, 0.9, 1.20 Å; sulfur atom, 0.34 Å<sup>3</sup>, 16, 1.80 Å. Carbon and hydrogen atom parameters are those used by Brant et al.,<sup>20</sup> while sulfur atom parameters are from Scheraga.<sup>19</sup> Intrinsic torsional potentials were  $(\Delta E_\phi/2)(1 - \cos 3\phi)$ , where  $\phi$  is taken to be zero for a trans placement. Barrier heights were 2.8 kcal mol<sup>-1</sup> for C-C bonds<sup>17</sup> and 2.0 kcal mol<sup>-1</sup> for C-S bonds.<sup>19</sup> Conformational energies were calculated at 10° intervals for variable dihedral angles. Terminal methyl groups were always oriented to yield a trans

placement for H-C-S-C or H-C-C-S, the hydrogen atom being that of the methyl group in question.

**Conformational Energy Maps.** Conformational energy maps for  $-\text{SCH}_2\text{CH}_2\text{SCH}_3$  and  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$  are depicted in Figures 1a and 1b, respectively. Boltzmann factors,  $\exp(-E_{\varphi_i\varphi_j}/RT)$ , were summed at  $10^\circ$  intervals for  $\varphi_i$  and  $\varphi_j$  over the regions assigned to trans (t) and gauche (g) states. For this purpose  $\varphi_i$  was defined as being in a t,  $g^+$ , or  $g^-$  state when it was within  $60^\circ$  of 0, 120, or  $-120^\circ$ , respectively. The temperature was 300 K. Summed Boltzmann factors differed by only about 3% for tt,  $tg^\pm$ , and  $g^\pm t$  states in  $-\text{SCH}_2\text{CH}_2\text{SCH}_3$  (Figure 1a). First-order interactions are therefore approximately identical in trans and gauche states. The difference in these interactions was also found to be small in the model described in Abe's preliminary report.<sup>14</sup> This situation is different from that encountered with poly(oxyethylene), for which first-order interactions are quite dissimilar in trans and gauche states.<sup>21</sup> The greater length of the C-S bond (1.82 vs. 1.43 Å for C-O) can be held responsible for the reduced importance of first-order interactions in the sulfur-containing polymers.

Repulsive second-order interactions occur when adjacent bonds adopt gauche states. These interactions are more severe for  $g^\pm g^\mp$  than for  $g^\pm g^\pm$  states, and they become more repulsive on going from a C-C, C-S pair to a C-S, S-C pair. Second-order interaction of the methyl groups in the latter case causes a pronounced displacement and splitting of the  $g^\pm g^\mp$  minimum (Figure 1b). Evaluation of summed Boltzmann factors for the  $g^\pm g^\pm$  and  $g^\pm g^\mp$  regions permits formulation of the statistical weight matrices (1) and (2).

$$U_{\text{C-C}} = U_{\text{C-S}} = \begin{bmatrix} 1.00 & 1.00 & 1.00 \\ 1.00 & 0.71 & 0.17 \\ 1.00 & 0.17 & 0.71 \end{bmatrix} \quad (1)$$

$$U_{\text{S-C}} = \begin{bmatrix} 1.00 & 1.00 & 1.00 \\ 1.00 & 0.33 & 0.07 \\ 1.00 & 0.07 & 0.33 \end{bmatrix} \quad (2)$$

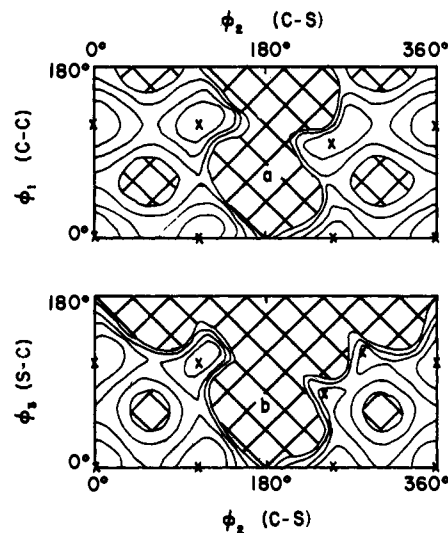
First-order interactions have been assumed identical in all states. Columns index the state of the bond in question, rows index the state of the preceding bond, and the order of indexing is t,  $g^+$ ,  $g^-$ . Dihedral angles associated with these states are 0, 120, and  $-120^\circ$ , respectively.

A priori and conditional probabilities were formulated from these statistical weight matrices, using the appropriate rotational isomeric state formalism.<sup>22</sup> The fractions of internal bonds adopting trans placements in a long, unperturbed acyclic chain are found to be 0.58 (C-S) and 0.50 (C-C). Conditional probabilities are the probability that bond  $i$  will adopt state  $\eta$ , given that the preceding bond is in state  $\xi$ . These probabilities, in matrix form, are (3)–(5).

$$\text{C-C bond} \begin{bmatrix} 0.414 & 0.293 & 0.293 \\ 0.616 & 0.310 & 0.074 \\ 0.616 & 0.074 & 0.310 \end{bmatrix} \quad (3)$$

$$\text{C-S bond} \begin{bmatrix} 0.480 & 0.260 & 0.260 \\ 0.676 & 0.260 & 0.062 \\ 0.676 & 0.072 & 0.260 \end{bmatrix} \quad (4)$$

$$\text{S-C bond} \begin{bmatrix} 0.427 & 0.287 & 0.287 \\ 0.788 & 0.175 & 0.037 \\ 0.788 & 0.037 & 0.175 \end{bmatrix} \quad (5)$$



**Figure 1.** Conformational energy maps for (a)  $-\text{SCH}_2\text{CH}_2\text{SCH}_3$  and (b)  $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$ . Local minima are denoted by  $\times$ . Contours are drawn at 1, 2, 3, and 4 kcal mol $^{-1}$  relative to the minimum energy. The conformational energy exceeds 4 kcal mol $^{-1}$  in the cross-hatched region. A trans placement is defined to have a dihedral angle of  $0^\circ$ .

Average configuration-dependent properties for acyclic poly(thiaethylenes) were evaluated from a representative sample of chains generated using the above a priori and conditional probabilities. Each sample contained 50 000–99 000 chains. The strategy involved in selecting cyclic chains from each representative sample was that utilized in the study of cyclic poly(oxyethylene).<sup>10</sup> Different tolerances for  $\Delta r$  and  $\Delta\theta$  were required, as will be seen below. Here  $r$  is the distance from the first to the last sulfur atom in an acyclic chain. It would be zero if the acyclic chain were to form a macrocycle containing one less heteroatom. The departure from  $102^\circ$  of the angle between the first S-C and last C-S bond in the acyclic chain is denoted by  $\Delta\theta$ . Its value would be close to  $0^\circ$  in the macrocycle.<sup>10,15</sup>

#### Average Properties of Acyclic and Cyclic Molecules

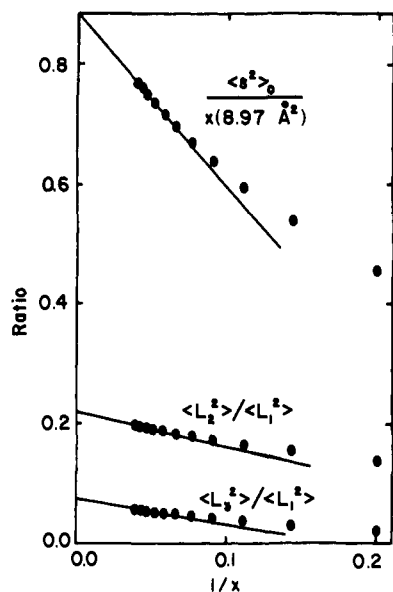
**Acyclic Chains.** The spatial distribution of sulfur atoms was characterized by computation of the moment of inertia tensor,  $S_{x2}$ , for each chain generated:

$$S_{x2} = x^{-1} \sum \mathbf{r}^{\times 2} - x^{-2} (\sum \mathbf{r})^{\times 2} \quad (6)$$

Here  $\mathbf{r}$  is the vector from the first sulfur atom to another sulfur atom. Summations extend over all  $x$  sulfur atoms, and  $\times 2$  as a superscript denotes the self-direct product. This procedure generates  $S_{x2}$  as a column comprised of the nine elements in reading order.<sup>23</sup> The principal moments are  $L_1^2 \geq L_2^2 \geq L_3^2$ . Values obtained by averaging corresponding moments over all chains in a sample are denoted by angle brackets. Their sum is the mean-square unperturbed radius of gyration,  $\langle s^2 \rangle_0$ .

Chain-length dependence of the characteristic ratio, defined here to be  $\langle s^2 \rangle_0/x$  (8.97 Å $^2$ ), is depicted in Figure 2. (Summation of squared lengths for two C-S and one C-C bonds yields 8.97 Å $^2$ .) A limiting value of about 0.88 is obtained as  $x$  goes to infinity, corresponding to  $(\langle r^2 \rangle_0/nl^2)_\infty = 5.3$ . The value obtained by Abe<sup>14</sup> for this ratio is somewhat lower, the difference presumably arising from slightly different statistical weights. Our result for  $(\langle r^2 \rangle_0/nl^2)_\infty$  is also slightly higher than the value of 4.2 found for poly(oxyethylene).<sup>21</sup>

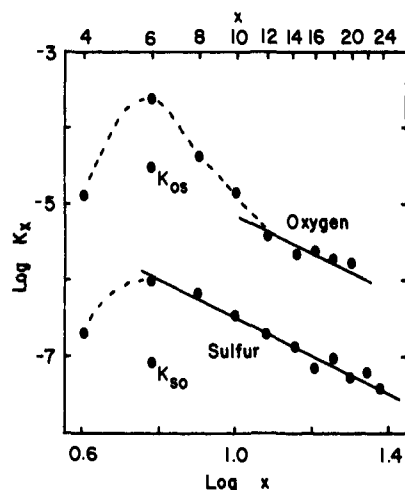
Asymmetry of individual configurations is assessed through examination of  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ . These ratios would be unity if all configurations had a spherically symmetric distribution of chain atoms about the center of gravity. On the other hand, both ratios would be zero if all chains were rods



**Figure 2.** Dependence of the characteristic ratio and ratios of averaged principal moments of the inertia tensors on the number of sulfur atoms,  $x$ , for unperturbed acyclic  $\text{CH}_3\text{S}(\text{CH}_2\text{CH}_2\text{S})_{x-1}\text{CH}_3$ . The sum of the squared length of two C-S and one C-C bonds is  $8.97 \text{ \AA}^2$ .

with a vanishingly small cross section. Large unperturbed chains on a cubic lattice,<sup>24-26</sup> as well as rotational isomeric state models for poly(methylene)<sup>27</sup> and poly(oxyethylene)<sup>10</sup> of infinite molecular weight, have  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  near 0.226 and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$  near 0.082.<sup>28</sup> Short poly(methylene) and poly(oxyethylene) chains have smaller values for these chains than those obtained as the number of bonds approaches infinity. Figure 2 depicts the behavior of  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$  for poly(thiamethylene). Each ratio increases with  $x$ , attaining limiting values in harmony with those found previously for other large, flexible, unperturbed acyclic chains. Substitution of sulfur for oxygen atoms in a long acyclic poly(oxyethylene) has no effect on the asymmetry of the spatial distribution and only a minor effect on the characteristic ratio.

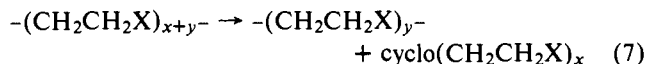
**Ease of Cyclization.** In a recent treatment of poly(oxyethylene), chains in a representative sample were considered to have cyclized to form  $(\text{CH}_2\text{CH}_2\text{O})_6$  if terminal oxygen atoms were separated by no more than  $0.55 \text{ \AA}$  and the angle between the first O-C and last C-O bond was  $110 \pm 2^\circ$ .<sup>10</sup> Such exacting criteria were adopted because the poly(oxyethylene) chain is nearly constrained to follow a diamond lattice in the rotational isomeric state model used to represent the actual conformations accessible to the molecule. Slight departures from this lattice arise because C-O and C-C bonds differ by  $0.10 \text{ \AA}$  in length and bond angles are displaced  $0.5^\circ$  from the tetrahedral angle. According to these criteria, 0.12% of the acyclic  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$  chains generated cyclize to form  $(\text{CH}_2\text{CH}_2\text{O})_6$ . In marked contrast, not even one  $\text{CH}_3\text{S}(\text{CH}_2\text{CH}_2\text{S})_6\text{CH}_3$  chain in a representative sample of 99 000 could fulfill these stringent criteria for cyclization. Criteria for successful cyclization must therefore be relaxed when treating the sulfur-containing polymers. After several trial calculations, the criteria were set at  $(\Delta r)^2$  less than  $\langle r^2 \rangle_{\text{rf}}/8$  and  $\Delta\theta < 45^\circ$ . Here  $\langle r^2 \rangle_{\text{rf}}$  is the random flight mean-square end-to-end distance. These criteria are sufficiently lax so that they are satisfied by a reasonable fraction of the chains generated. However, these criteria are also sufficiently exacting to yield  $\langle s^2 \rangle_{0,\text{cyclic}} / \langle s^2 \rangle_{0,\text{acyclic}}$  near the theoretically expected<sup>29</sup> value of  $1/2$  for large polymers, the ratio being evaluated for polymers containing the same number of sulfur atoms. Specifically, polymers with 8, 10, . . . , 24 sulfur atoms in the macrocycle have an average of 0.51 for



**Figure 3.** Cyclization constants for  $(\text{CH}_2\text{CH}_2\text{X})_x$ , where X is either an oxygen or sulfur atom. The points denoted  $K_{\text{SO}}$  and  $K_{\text{OS}}$  are discussed in the text.

$\langle s^2 \rangle_{0,\text{cyclic}} / \langle s^2 \rangle_{0,\text{acyclic}}$ . The excellent agreement between this value and the result of  $1/2$ , anticipated from theoretical considerations, justifies extraction of conformational properties for poly(thiamethylene) macrocycles from those chains fulfilling the criteria for cyclization.

Cyclization constants<sup>15,30,31</sup>  $K_x$  for the reaction



X = sulfur or oxygen, were estimated as

$$K_x = 3N_{\text{cyc}}[4\pi N L \sigma_{\text{cx}}(\Delta r)_{\text{max}}^3]^{-1} \quad (8)$$

Here  $N_{\text{cyc}}$  out of  $N$  chains in a representative sample satisfy the criteria for cyclization,  $\Delta r_{\text{max}}$  is the maximum value of  $\Delta r$  for a cyclic chain,  $L$  is Avogadro's number, and  $\sigma_{\text{cx}}$  is the symmetry number for the cyclic molecule. The definition of  $K_x$  shows that it is an equilibrium constant for a cyclization reaction in which end groups are conserved. Values of  $N_{\text{cyc}}N^{-1}(\Delta r)_{\text{max}}^{-3}$  for poly(oxyethylene) were obtained from data reported in ref 10, while those for poly(thiaethylene) are from the Monte Carlo calculations reported in the present work. Consequently much more severe constraints for  $\Delta r$  and  $\Delta\theta$  apply in calculation of  $K_x$  for poly(oxyethylene). Results are depicted in Figure 3.

Poly(oxyethylene) has a greater propensity for cyclization than does poly(thiaethylene) at all  $x$  for which results are depicted in Figure 3. This calculated result is in qualitative agreement with yields obtained in syntheses.<sup>8,9</sup> Termini of poly(thiaethylene) chains are less likely than termini of poly(oxyethylene) of the same  $x$  to have the small separation and proper angular disposition required for macrocycle formation.

Theoretical considerations justify the expectation that  $K_x$  should become proportional to  $x^{-5/2}$  at sufficiently high  $x$ .<sup>15</sup> Solid straight lines in Figure 3 are drawn with a slope of  $-5/2$ . A line with this slope provides a reasonable fit to the  $K_x$  for macrocycles containing six or more sulfur atoms. The oxygen-containing macrocycles must be substantially larger before the limiting behavior is obtained. It is not convincingly clear that the limiting behavior is reached for oxygen-containing macrocycles with 20 oxygen atoms.

In each series the cyclization constant goes through a maximum when the product macrocycle contains six heteroatoms. The maximum in the series of sulfur-containing polymers does not, however, imply anything remarkable about  $(\text{CH}_2\text{CH}_2\text{S})_6$  because  $K_6$  lies on the straight line whose slope is  $-5/2$ . A maximum occurs at  $x = 6$  because  $K_4$  falls far

below the value obtained by extrapolation of the straight line. The ratio of the calculated  $K_4$  and  $K_6$  is in reasonable agreement with the observation that reaction of  $\text{HSCH}_2\text{CH}_2\text{SH}$  and  $\text{BrCH}_2\text{CH}_2\text{Br}$  yields nine times more  $(\text{CH}_2\text{CH}_2\text{S})_6$  than  $(\text{CH}_2\text{CH}_2\text{S})_4$ .<sup>9</sup> This result provides additional evidence that criteria adopted for cyclization are sufficiently rigorous to permit a reasonably accurate assessment of the properties of poly(thiamethylene) macrocycles.

A somewhat different situation is obtained in the series of oxygen-containing polymers. As in the sulfur-containing series,  $K_4$  lies below the value obtained by extrapolation of the solid line. However, in the oxygen-containing series  $K_6$  is well above the value predicted by extrapolation. Certain frequently occupied chain conformations for  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$  yield an orientation of terminal bonds conducive to cyclization. A notable example is  $(-\text{tg}^{\pm}\text{t}-\text{tg}^{\mp}\text{t}-)_3$  with gauche placements occurring at the C-C bonds.<sup>10</sup>

Two factors contribute to the pronounced difference in cyclization constants for molecules containing six heteroatoms. First, the C-X bond length, as well as the C-C-X and C-X-C angles, depends on whether X is an oxygen or sulfur atom. Second, statistical weights, and hence the a priori and conditional probabilities, depend on the identity of the heteroatoms. The relative importance of these two factors was assessed by computation of four  $K_{XY}$ , defined as the cyclization constants at  $x = 6$  for the chain whose backbone geometry is that of poly( $\text{CH}_2\text{CH}_2\text{X}$ ), while statistical weights are those appropriate for poly( $\text{CH}_2\text{CH}_2\text{Y}$ ). Tolerances for cyclization were those described above for poly( $\text{CH}_2\text{CH}_2\text{X}$ ). The results,  $K_{OO} > K_{OS} > K_{SS} > K_{SO}$ , are depicted in Figure 3. The two largest cyclization constants are obtained with poly(oxyethylene) chain geometry. The greater difficulty in cyclization of poly(thiaethylene) at  $x = 6$  can be attributed primarily to the increase in C-X bond length and alteration of C-X-C and C-C-X angles when X is changed from an oxygen to a sulfur atom.

**Alteration of Unperturbed Dimensions upon Cyclization.** As the ring size increases,  $\langle s^2 \rangle_{0,\text{cyclic}} / \langle s^2 \rangle_{0,\text{acyclic}}$  approaches  $1/2$ .<sup>29</sup> This ratio is 0.515 (standard deviation 0.018) for macrocycles containing 6, 8, . . . , 24 sulfur atoms. Nearly the same result, 0.50 (standard deviation 0.04), was obtained for macrocycles containing 6, 8, . . . , 20 oxygen atoms.<sup>10</sup> Thus the alteration in unperturbed dimensions upon formation of macrocycles of moderate size is essentially that expected for large rings. Unperturbed dimensions for  $(\text{CH}_2\text{CH}_2\text{S})_x$  will be larger than those for  $(\text{CH}_2\text{CH}_2\text{O})_x$  because the sulfur-containing polymers have slightly higher characteristic ratios and greater mean-squared bond lengths.

**Alteration in Asymmetry upon Cyclization.** Figure 4 depicts  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$  for  $(\text{CH}_2\text{CH}_2\text{S})_x$  with even  $x$  from 6 to 24. Scatter is greater than that seen for acyclic chains (Figure 2) because comparatively few of the chains generated fulfill requirements for successful cyclization. Cyclization causes a substantial increase in both principal moment ratios. This increase is most dramatically exhibited by  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  for the smaller macrocycles. It persists even for the poly(thiaethylene) with 24 sulfur atoms. Both  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$  nearly double upon cyclization of this molecule. Cyclization at  $x = 24$  causes a 60% reduction in  $\langle L_1^2 \rangle$  but only about a 25% reduction in  $\langle L_2^2 \rangle$  and  $\langle L_3^2 \rangle$ . Similar results are obtained with poly(oxyethylene).<sup>10</sup> As the number of bonds in a macrocycle approaches infinity, the values of  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and  $\langle L_3^2 \rangle / \langle L_1^2 \rangle$  approach 0.37 and 0.155, respectively.<sup>28</sup>

The unperturbed triglycerides of human chylomicrons and very low density lipoproteins represent another class of molecules with low asymmetries. Values of  $\langle L_2^2 \rangle / \langle L_1^2 \rangle$  and

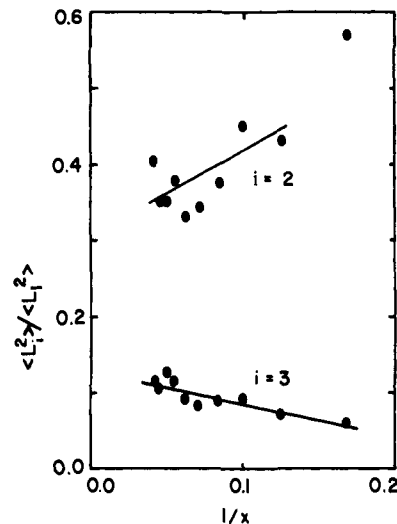


Figure 4. Ratios of averaged principal moments of the inertia tensors for  $(\text{CH}_2\text{CH}_2\text{S})_x$ .

$\langle L_3^2 \rangle / \langle L_1^2 \rangle$  are  $0.32 \pm 0.02$  and  $0.08 \pm 0.01$ , respectively, for such triglycerides.<sup>32</sup> These ratios bear a resemblance to those found here for poly(thiaethylene) macrocycles of comparable molecular weight ( $x$  ca. 14). In one case the low asymmetry arises from cyclization, while in the other it can be attributed to the branched nature of the molecule.<sup>28,32,33</sup>

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