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Equilibrium ring concentrations and the statistical conformations of polymer chains
Part 15. Large cyclics in liquid sulfur

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Abstract

A rotational isomeric state (RIS) model for polymeric sulfur chains has been used to calculate the concentrations of cyclics S_x with $x > 8$ in liquid sulfur below the critical polymerization temperature. The cyclics S_{12}, S_{18} and S_{20} were predicted to be present in the largest amounts in agreement with experiment. Other cyclics such as S_{11} and S_{13} were predicted to be absent from the melt and they are known to be physically present in only trace amounts. Variations of structural and statistical weight parameters in the RIS model are explored. The original model is shown to give the best agreement with all experimental information.

Keywords: Liquid sulfur; Large cyclics; Rotational isomeric state model

1. Introduction

The molecular constitution of liquid sulfur has been the subject of experimental investigation and theoretical speculation for well over a hundred years, in fact ever since the discovery of the self-depression of its freezing point by Gernez [1]. When heated from its melting point to its boiling point, the liquid element changes colour from pale yellow, to orange, then to red and finally to black. Above a critical polymerization temperature of 432 K, there is a large increase in viscosity associated with the formation of polymeric sulfur (called $S\mu$) [2–7]. Below this temperature and above the melting point, the liquid element consists of cyclooctasulfur S_8 (called $S\lambda$) together with sulfur species, known collectively as $S\pi$ (see, for example, Ref. [8–10]). Using Infrared and Raman spectroscopy and high performance liquid chromatography (HPLC), Steudel and his co-workers have established the identity of $S\pi$ [6,11]. It is a mixture of small cyclics S_6 and S_7 (as about 3.5% by weight) together with larger cyclics S_x with $x > 8$ (as about 1.5% by weight), the remaining 95% by weight being cyclooctasulfur [6,11]. Although Steudel and his co-workers demonstrated that large sulfur rings with at least 34 atoms are present at equilibrium in the liquid element, they were only able to isolate three sizes from the melt. These are S_{12}, S_{18} and S_{20} (see Ref. [12 and 13]) and they are the cyclics S_x with $x > 8$ that were shown to be present in the largest amount by HPLC [6]. Steudel et al. also used HPLC to show that some cyclics (such as S_{11} and S_{13}) were only present in trace amounts and also that the cyclic population extended up to and beyond S_{26}.

In this article, individual large ring concentrations in liquid sulfur are calculated using a well established rotational isomeric state (RIS) model [14–16] to describe the statistical conformations of the corresponding open chain molecules. The predictions of the RIS model are in good agreement with the experimental results of Steudel and his co-workers and the effect of varying the structural and statistical weight parameters of the model on the calculations are explained in detail.

2. The rotational isomeric state model

Polymeric sulfur (often called polycatenasulfur) has the simplest structure of any linear polymer. In Fig. 1, a section of the polymer is shown in the all *trans* state with bond angle supplements θ and internal rotation angles ϕ_{i-1} and ϕ_i. The S–S bond length l is assigned the value 0.206 nm and θ is assigned the value 74° from a wide range of structural data available in the literature [7,14].

Pauling [17,18] was the first to propose that the mutual

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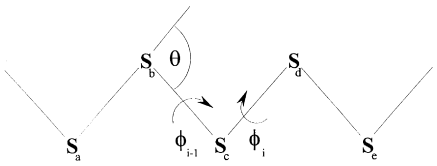

Fig. 1. A section of a polymeric sulfur chain with all its bonds in *trans* states.

repulsion of adjacent lone pairs of pπ-electrons give rise to two-fold torsional rotational potentials about sulfur–sulfur (and incidentally selenium–selenium) bonds. Minima in these potentials are located at $\phi = \pm 90°$ (where $\phi = 0°$ represents the *trans* state). The torsional barrier heights for disulphides are typically ca. 40 kJ mol^{-1}, which is much greater than RT mol^{-1} at the temperatures T relevant to this study of the cyclic content of liquid sulfur (where R is the gas constant). In consequence, each bond in a linear sulfur chain can be considered to be in one of the two discrete rotational isomeric states located at $\phi = +90°$ (a + state) or $\phi = -90°$ (a − state). With reference to Fig. 1, the statistical weight matrix $\mathbf{U}_i$, which takes account of the interdependence of bond rotational states, is then given by

$$\mathbf{U}_i = \begin{array}{c} \\ +\phi_{i-1} \\ -\phi_{i-1} \end{array} \begin{array}{c} \begin{array}{cc} +\phi_i & -\phi_i \end{array} \\ \begin{bmatrix} 1 & \sigma \\ \sigma & 1 \end{bmatrix} \end{array} \quad (1)$$

where the statistical weight parameter σ is the Boltzmann factor

$$\sigma = \exp^{-\Delta E/RT} \quad (2)$$

where ΔE is the energy difference between the states + − (or − +) and + + (or − −).

Now the distances between the centres of sulfur atoms separated by four chemical bonds in the + + (or − −) and + − (or − +) states lie in the range 0.619 – 0.357 nm. Since, the van der Waals diameter for non-bonded sulfur atoms is 0.360 nm [19], there should be net forces of attraction between S_a and S_e in all the states defined in Eq. (1) and so $\sigma > 1$. The best estimate of σ from empirical formulae representing van der Waals forces between non-bonded sulfur atoms [20,21] is -1.2 kJ mol^{-1} at temperatures between the melting point and critical polymerization temperature of elemental sulfur, so that $\sigma = 1.4$. However, for the initial calculation presented here, the relatively small attractive forces between non-bonded atoms of the sulfur chains (separated by four skeletal bonds) were neglected and σ was assumed to be unity.

The rotational isomeric state model (originally described in Ref. [14]) was used to calculate large ring concentrations in liquid sulfur as described in this article. The main structural and statistical parameters were then systematically varied to explore their effects on the calculated large ring concentrations. It is shown that even quite small changes to the parameters lead to major discrepancies with the experimental data and that the original rotational isomeric state model gives the best results, with good agreement with the experimental data of Steudel and his co-workers [7,11].

3. Cyclic concentrations in liquid sulfur below the critical polymerization temperature

The rotational isomeric state model described above was used to calculate cyclic concentrations in liquid sulfur. Following Gee [2,3] and Tobolsky and Eisenberg [22], equilibrium between molecules S_x and diradical chains in liquid sulfur may be represented as follows

$$S_y. \rightleftharpoons .S_{y-x}. + S_x \quad (3)$$

Molar cyclization equilibrium constants K_x are given by

$$K_x = \frac{[S_x][.S_{y-x}.]}{[.S_y.]} \quad (4)$$

If it is further assumed that there is a most probable distribution of chain lengths for the linear species, then

$$K_x = \frac{[S_x]}{(1 - 1/\bar{y})^x} \quad (5)$$

where $\bar{y}$ represents the average number of sulfur atoms in the chains.

For present purposes, it is assumed that

$$K_x \cong [S_x] \quad (6)$$

corresponding to substantial values of $\bar{y}$, although it is recognised that this may not be the case and absolute values of individual cyclic concentrations may be adjusted accordingly when reliable values of $\bar{y}$ are determined experimentally. Furthermore, there may be bond rearrangement reactions in liquid sulfur involving the formation of four centre transition states as postulated by Eisenberg [23]. Such bond interchange reactions could lead to ring–ring equilibria in liquid sulfur in addition to the ring–chain equilibria.

The small cyclics in liquid sulfur S_6 and S_7 have been shown to be strained [24-26] but it is assumed that rings with more than 8 sulfur atoms are unstrained, so that applying a modification of the Jacobson and Stockmayer [27] cyclization theory for non-Gaussian chains [28]

$$K_x = \frac{z}{Z(4/3)\pi r^3 N_A \sigma_{Rx}} \quad (7)$$

where Z represents the total sum of the statistical weights of all the individual conformations defined by the RIS model for an x-meric chain and z represents the sum of the statistical weights of those conformations that have the centres of their terminal atoms separated by less than a reaction distance r. The quantity N_A is the Avogadro constant and σ_{Rx} is a symmetry number, which is x for S_x rings [28].

Table 1

Value of x in S_x	Number of conformations corresponding to ring formation z	Total number of conformations Z
9	0	48
10	0	88
11	0	162
12	4	298
13	0	536
14	0	980
15	0	1790
16	0	3270
17	4	5974
18	16	10896
19	10	19832
20	68	36144
21	44	65724
22	74	119644
23	236	217716
24	248	395672
25	298	719284
26	634	1307670
27	1424	2376558
28	2134	4317352

The RIS model for sulfur chains was applied to calculate individual cyclic concentrations [S_x] with $x > 8$ by using Eq. (6). The statistical weight parameter σ in Eq. (1) was initially taken to be unity. An excluded volume corresponding to each sulfur atom in the chain having a finite volume was taken into account as follows. When the distances between the centres of non-bonded sulfur atoms (with the exception of the terminal pairs) were less than 0.3 nm, the conformations were not included in the calculation. Ring formation was assumed when the reaction distance r was less that 0.3 nm. The results of the calculation are listed in Table 1, which predicts that the cyclics S_x with $x > 8$ that are present in largest concentrations in liquid sulfur below the critical polymerization temperature are S_{12}, S_{18} and S_{20}. These are the only large rings to have been recovered from liquid sulfur. Furthermore, some cyclics such as S_9, S_{10}, S_{11}, S_{13}, S_{14}, S_{15} and S_{16} are predicted to be absent from the molten element. Steudel and his co-workers reported detecting all these cyclics but some were present in only trace quanties [11].

4. The predicted conformations of large sulfur rings

The RIS model enables the individual conformations of chains corresponding to rings to be examined and compared to the established crystal structures for homocyclic sulfur molecules. The crystal structures for S_{10}[29], S_{12}[30], α-S_{18}[31], β-S_{18}[32] and S_{20}[31] have been found by X-ray crystallography and are shown in Table 2 along with the values of bond lengths, bond angles and torsional angles in these structures. The conformations the model generated which would be expected to result in cyclization are shown in Table 3 and it can be seen that two of these match the crystal structures for S_{12} and α-S_{18}. It can be seen from Table 2 that S_{10}, β-S_{18} and S_{20} contain torsional angles that differ considerably from the values of $\pm 90°$ used in the RIS model and so it is not surprising that these conformations were not predicted. The conformations of the crystal structures for β-S_{18} and S_{20} were predicted by the model to have their ends close enough for cyclization but were not able to form as there was some overlap in the chains. In both cases this overlap was slight and could be easily alleviated by slight variations in the torsional angles, bond lengths and bond angles. The model also shows the conformation of S_{10} from the crystal structure, to have an end-to-end distance too large for cyclization and overlap also occurs in the chains. There would need to be considerable variation in the torsional angles, bond lengths and bond angles in order for the corresponding chain to cyclize. It should be noted that the conformations favoured in crystal structures need to be not only suitable to give stable cyclics, but also to pack well in the crystal lattice. However, when studying rings in the melt, this second criterion may be relaxed and different conformations may be favoured.

5. Effect of changing the structural and statistical weight parameters of the RIS model

The RIS model of polymeric sulfur presented here is based on a wide range of structural data and it was successful in calculating the mean dipole moments of some *n*-alkyl polysulfides [14]. The model correctly predicts that large cyclics S_{12}, S_{18} and S_{20} should be present in substantial

Table 2
Known crystal structures of S_x rings for $x > 8$. (See Ref. [7])

S_x	Conformation	Torsion angles ϕ(°)	Bond angle supplements θ(°)	Bond lengths l(nm)
S_{10} [29]	− + − − + − + − − +	56.3–104.6	69.8–76.7	0.203–0.208
S_{12} [30]	+ + − − + + − − + + − −	90.6–94.0	72.6–74.6	0.205–0.206
α-S_{18} [31]	+ − − + + − + + + − + + − − + − − −	91.0–100.5	71.7–76.2	0.204–0.207
β-S_{18} [32]	+ + − + − − + + + − − + − + + − − −	92.2–113.5	70.7–75.8	0.205–0.210
S_{20} [31]	+ + + + − + + + + − + + + + − + + + + −	90.1–113.7	72.3–75.4	0.202–0.210

Table 3
S_x conformations predicted to cyclize for $8 < x < 20$

S_x	Conformation	No of conformations
S_{12}	+ − − + + − − + + [a]	4
S_{17}	+ + + − + + − − + − − − − +	4
S_{18}	+ + + + − − + + − − − − − + +	4
	+ − − + + − + + + − + + − − + [b]	2
	+ − − + + − − − − − + + − − +	2
	+ − − − − − + + − − + + + + +	4
	+ − − + + − − − − + − − + + −	4
S_{19}	+ + + + − + + + + − + + + + − +	4
	+ + + − + + + + − + + + + − + +	4
	− + + + + − + + + + − + + + + −	2

[a] Conformation corresponding to the crystal structure of S_{12}.
[b] Conformation corresponding to the crystal structure of α-S_{18}.

quantities in liquid sulfur and it predicts very low concentrations of the cyclics S_{11} and S_{13} as found experimentally [7,11]. Furthermore, with excluded volume effects taken into account, the model predicts all the cyclics with more than 17 skeletal bonds to be present in liquid sulfur, with a general decrease in concentrations from S_{20} to S_{26} in agreement with the HPLC data [7,11]. If cyclic concentrations are equated with molar cyclization equilibrium constants (see Eq. (6)) the total ring content from S_9 to S_{26} is calculated to be about 0.7% by weight. More cyclics up to at least S_{34} are believed to be present in liquid sulfur, so here again there is satisfactory agreement between theory and experiment (Steudel [7,11] estimates cyclics S_x with $x > 8$ to be present as about 1.5% by weight in liquid sulfur below the critical polymerization temperature).

Two factors that were not taken into account in the calculation were possible ring–ring equilibrium reactions and any correlation between the termini of chains forming rings in liquid sulfur. The latter factor has been discussed for other synthetic polymers by Flory and his co-workers [33-36].

The main structural and statistical weight parameters were systematically varied in order to explore the effect on the calculated large ring concentrations. The results of this procedure are now outlined.

5.1. The statistical weight parameter σ.

When $1 < \sigma < 2$ (see Eqs. (1) and (2)), a good correlation with the experimental data was achieved. However, when σ was set equal to 3, the concentration of S_{21} was predicted to be larger than S_{20}, although it is the latter that has been recovered from quenched molten sulfur [7,11]. A value of $\sigma = 1.4$ is believed to be the best estimate available [14] and was used in the following three calculations (5.2, 5.3 and 5.4).

5.2. The internal rotation angle ϕ.

When the value of ϕ was changed by just $\pm 10°$, the cyclic S_{12} was predicted to be absent from the melt. Furthermore, when $\phi = \pm 80°$, S_{18} and S_{20} were no longer predicted to be major components and when $\phi = \pm 100°$, no S_{18} was predicted. This reinforced the view $\phi = \pm 90°$, that gives the best correlation with experiment.

5.3. The reaction distance r.

The original estimate of 0.3 nm for the reaction distance r between chain terminal atoms forming rings (see above) gave a good fit with the available experimental data. Use of a reaction distance of $r = 0.35$ nm caused deviation from the experimental data as S_{17} and S_{19} were present in larger concentrations than S_{18} and S_{20}. When r was set equal to 0.25 nm, the cyclic S_{12} was predicted to be absent from the melt.

5.4. The excluded volume distance d.

In the RIS model used, conformations of chains with the distances d between the centres of non-bonded sulfur atoms within the chains that were separated by less than 0.3 nm were not included in the calculated ring concentrations. When this distance was increased to 0.33 nm, all the conformations became excluded, as this is greater than the distance between atoms separated by two bonds. When d was decreased to 0.265 nm, substantial quantities of S_{13} were predicted in direct contradiction to the experimental information [7,11].

6. Conclusions

The simple RIS model for polymeric sulfur used here gives large ring concentrations in liquid sulfur in good agreement with all the available experimental data. Its unique simplicity allows for a detailed exploration of the effect of varying structural and statistical weight parameters. The success of the model gives encouragement for future attempts to correlate large cyclic concentrations in polymeric systems with the statistical conformations of the corresponding open chain molecules. Even more detailed calculations of ring concentrations in liquid sulfur may be possible following more experimental data being obtained relating to this imperfectly understood but fascinating chemical element.

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