Solvothermal Routes to Poly(carbon monosulfide)s Using Kinetically Stabilized Precursors

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The search for simple compositions in the area of carbon chemistry, e.g., the carbon nitrides1 and the fullerens,2 has proven especially fruitful. In this spirit, we have been investigating the chemistry of the carbon sulfides, focusing on simple neutral and anionic species.3,4 Carbon sulfides are attractive because they are derived from inexpensive feedstocks and the neutral and anionic species.3,4 Carbon sulfides are attractive precursors should give products of the formula \([\text{C}_4\text{S}]_n\). In this spirit, we have been investigating whether the structural relationships between the precursors and products, if any, is subject to little control.

The requisite \(\text{C}_4\text{S}_x\) precursors were obtained by two independent routes, shown in Scheme 1. The bis(dithiocarbamate) \(\text{C}_4\text{S}_6\text{O}_2\) undergoes hydrolysis upon treatment with 4 equiv of NaOMe (MeOH solution, 3 days, 25 °C). Addition of \(\text{PPH}_4\text{Cl}\) to an aqueous extract of this material gave reddish brown microcrystals of approximate composition \(\text{PPH}_4\text{C}_4\text{S}_6\text{O}_2\) (\(x \approx 5\)). (1) An alternative route to the same precursor begins with the reaction of hexachlorobutadiene with a DMF solution of \(\text{Na}_2\text{S}\) (3 equiv, 30 min, 85 °C) to give a brown precipitate of the approximate composition \(\text{C}_4\text{S}_6\). It is likely that this material is related to Fanghanel’s molecular \(\text{C}_4\text{S}_6\), although our material is insoluble in common solvents. Suspensions of \(\text{C}_4\text{S}_6\) dissolve in anhydrous ammonia upon treatment with 2 equiv of sodium. Evaporation of these solutions followed by treatment of an aqueous extract with \(\text{PPH}_4\text{Cl}\) gave I, the nature of which is the subject of ongoing studies.

The first new polymer was synthesized by the condensation of I in the presence of a small amount of MeCN solvent (1 mL/g of I) in a thick-walled Pyrex tube (6 h, 90 °C). Upon cooling, one obtains black crystals of 2 (76% yield). These were analyzed by energy dispersive X-ray fluorescence (EDX) which showed that the P/S ratio was 1.4.13 Single-crystal X-ray diffraction analysis of 2 revealed a remarkable structure consisting of one-dimensional chains of \(\text{C}_4\text{S}_6\) units interconnected by S–S bonds (Figure 1).14 The \(\text{C}_4\text{S}_6\)– chains run along the crystallographic c-axis, and within each chain the tricyclic subunits are related by c2 glide-reflections. The chains are well separated by the \(\text{PPh}_4^+\) cations. The \(\text{C}_4\text{S}_6\) subunits are of idealized \(D_{2d}\) symmetry, being comprised of a pair of thioene rings fused to a central 1,4-dithiin (\(\text{C}_4\text{S}_2\)) ring.

Scheme 1

![Scheme 1](image_url)


7. (1) IR (KBr, \(\text{PPh}_4^+\) salts excluded): 1439 (\(\nu(C=C)\) and 1024 cm\(^{-1}\) (\(\nu(S=S)\).


10. (12) IR (KBr, \(\text{PPh}_4^+\) salts excluded): 1439 (\(\nu(C=C)\) and 1024 cm\(^{-1}\) (\(\nu(S=S)\).

Figure 1. Top: structure of the C₈S₈²⁻ subunit. Selected distances (Å): S1–C7, 1.701(6); S2–C4, 1.714(6); S2–S7, 2.132(2); S4–C3, 1.744(6); S4–C2, 1.761(6); S5–C1, 1.731(6); S5–C8, 1.733(6); S6–C5, 1.767(6); C1–C2, 1.399(8); C2–C6, 1.401(8); C6–C8, 1.385(8).

Bottom: structure of the [C₈S₈]₂⁻ chain in (PPh₄)₂C₈S₈·MeCN, viewed down the a-axis.

Solutions of 2 in dimethylformamide (DMF) are deep green, which is atypical for carbon sulfides.16 The electrical conductivity of DMF solutions of 2 are consistent with a 2:1 electrolyte,17 indicating that 2 depolymerizes upon dissolution. The fully dissociated state of the polymer is also indicated by the fact that the UV-vis spectrum obeys Beer’s Law over the range of 7.27 × 10⁻⁴ to 7.36 × 10⁻⁶ M. Compound 2 is diamagnetic in the solid state but paramagnetic in DMF solution. The paramagnetism was first indicated by an inability to observe the ¹³C NMR signals for anything but the PPh₄⁺ cation for DMF extracts of 2. The EPR spectrum of DMF extracts of 2 at room temperature shows a strong isotropic signal at g = 2.023. The magnetic moment of DMF solutions, as determined by the Evans method, is 1.4 µB per C₈S₈²⁻ unit.

The electrochemical properties of 2 are rich, as the heterocycle undergoes both oxidation and reduction. Cyclic voltammetry experiments reveal a pair of quasi-reversible reductions at −720 and −1080 mV (all potentials referenced to Ag/AgCl).18 Oxidation of (PPh₄)₂C₈S₈ occurs at −0.9 V and appears to be irreversible. The irreversibility may be attributed to the slow kinetics of the intermolecular S–S bond-making and bond-breaking process as well as the insolubility of the resulting [C₈S₈]₂⁺.

Electroactive sulfur-rich polymers have attracted recent attention as cathode materials in lithium ion batteries.19 In summary, well-defined carbon sulfide polymers have been prepared via the stepwise assembly from preformed C₈S₈ precursors. The anionic polymer dissociates in DMF to give an inorganic tricycle exhibiting rich optical, electrochemical, and chemical properties. Given the large number of carbon sulfido precursors available,3,4 it is likely that solvothermal methods could be fruitfully applied to the synthesis of related C–S materials.

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Supporting Information Available: Experimental procedures and crystallographic information (tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles, 19 pages). See any current masthead page for ordering and Internet access instructions.

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