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

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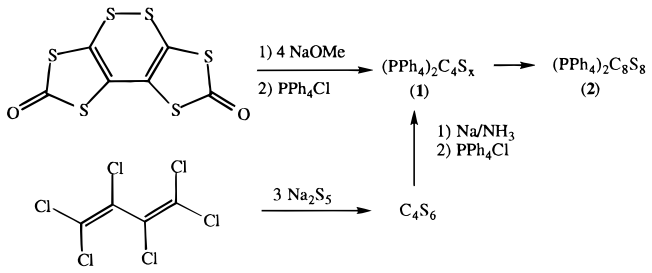
The search for simple compositions in the area of carbon chemistry, e.g., the carbon nitrides[1] and the fullerenes,[2] has proven especially fruitful. In this spirit, we have been investigating the chemistry of the carbon sulfides, focusing on simple neutral and anionic species.[3,4] Carbon sulfides are attractive because they are derived from inexpensive feedstocks and the constituent elements are known to form thermochemically robust linkages, thus making it possible to create structurally complex, kinetically stable inorganic polymers.[5] Carbon sulfide polymers are synthesized via exotic precursors (CS[6] and C_3S_2[7]) or highly specialized conditions, e.g., CS_2 is polymerized on a submilligram scale at 45 kbar (175 °C).[8] The resulting polymeric materials—poly(CS), poly(CS_2), and poly(C_3S_2)—are relatively poorly defined. Alternative forms of carbon sulfides have been discussed in the context of theoretical calculations and mass spectrometric measurements.[9] This paper describes the solvatothermal synthesis[10] of compositionally pure and structurally well-defined carbon sulfides.

A key aspect of our strategy is the use of kinetically robust C_4S_x fragments. Given their substantial strength, the C—C linkages in our precursor reagents were expected to survive the relatively aggressive conditions characteristic of solvatothermal processing, *ensuring that the microstructure of the product be related to the molecular structure of the precursor*. Thus, C_4S_x precursors should give products of the formula $[C_4S_y]_n$. In contrast, the precursors used in most solvatothermal reactions degrade upon exposure to the highly nucleophilic mineralizers (e.g., OH^-, S_x^{2-}). While previous flux and solvatothermal methods have been indisputably fruitful,[11] the structural relationship between the products and precursors, if any, is subject to little control.

Scheme 1



The requisite C_4S_x precursors were obtained by two independent routes, shown in Scheme 1. The bis(dithiocarbonate) $C_6S_6O_2$[3c] undergoes hydrolysis upon treatment with 4 equiv of NaOMe (MeOH solution, 3 days, 25 °C). Addition of PPh_4Cl to an aqueous extract of this material gave reddish brown microcrystals of approximate composition $(PPh_4)_2C_4S_x$ ($x \approx 5$) (**1**). An alternative route to the same precursor begins with the reaction of hexachlorobutadiene with a DMF solution of Na_2S_5 (3 equiv, 30 min, 85 °C) to give a brown precipitate of the approximate composition C_4S_6. It is likely that this material is related to Fanghänel's molecular C_4S_6,[12] although our material is insoluble in common solvents. Suspensions of C_4S_6 dissolve in anhydrous ammonia upon treatment with 2 equiv of sodium. Evaporation of these solutions followed by treatment of an aqueous extract with PPh_4Cl gave **1**, the nature of which is the subject of ongoing studies.

The first new polymer was synthesized by the condensation of **1** in the presence of a small amount of MeCN solvent (1 mL/g of **1**) 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 $C_8S_8^{2-}$ units interconnected by S−S bonds (Figure 1).[14] The $[C_8S_8]_n^{2n-}$ chains run along the crystallographic *c*-axis, and within each chain the tricyclic subunits are related by *c*/2 glide-reflections. The chains are well separated by the PPh_4^+ cations. The C_8S_8 subunits are of idealized D_{2h} symmetry, being comprised of a pair of thiophene rings fused to a central 1,4-dithiin (C_4S_2) ring. The tricyclic moiety exhibits a slight folding of 2.1° along the S···S axis of the dithiin. The S−S linkages between the rings involve sulfur atoms that are trans on the tricyclic core. The S−S distances of 2.167(6) Å are *ca.* 5% longer than the narrow range typical for S−S bonds (e.g., 2.051 Å in S_8[15]). This elongation suggests that the S−S bonds are weak, as borne out by the solution properties of this material.

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(13) IR (KBr, PPh_4^+ bands excluded): 1439 (νC=C) and 1024 cm^{-1} (νC=S).

(14) Single-crystal X-ray diffraction data were collected at 198 K on a Siemens 3-circle platform diffractometer with CCD area detector. Crystal data for $(PPh_4)_2[C_8S_8]\cdot CH_3CN$: monoclinic $P2_1/c$ (No. 14), $a = 12.8619(5)$ Å, $b = 21.9465(8)$ Å, $c = 18.3186(8)$ Å, $\beta = 96.541(2)°$, $V = 5137.2(4)$ Å^3, $Z = 4$, $d_{calcd} = 1.383$ g/cm^3, $2\theta_{max}$ (Mo Kα) = 50.10. Unique data: 9080. Data with $F_o^2 > 4\sigma(F_o^2)$: 4377 (622 variables). Final $R = 7.18\%$ ($wR_2 = 11.69\%$).

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S0002-7863(97)00042-5 CCC: $14.00

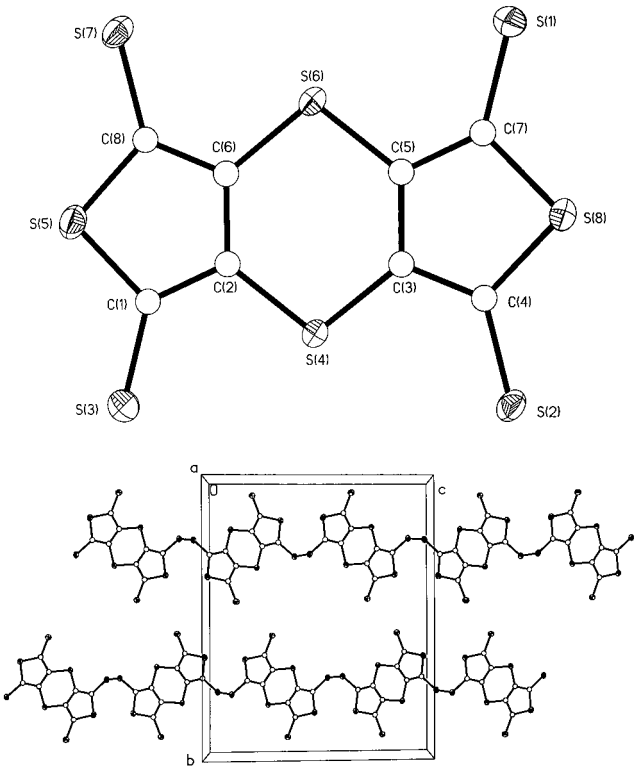
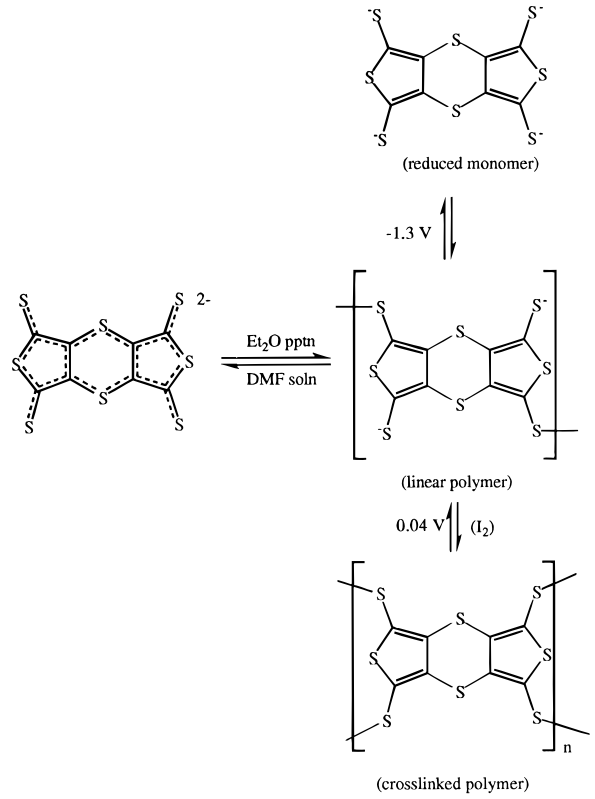


Figure 1. Top: structure of the $C_8S_8^{2-}$ subunit. Selected distances (Å): S1−C7, 1.701(6); S2−C4, 1.714(6); S2−S7, 2.132(2); S4−C3, 1.744(6); S4−C2, 1.761(6); S5−C1, 1.731(6); S5−C8, 1.733(6); S6−C5, 1.767(6); C1−C2, 1.399(8); C2−C6, 1.401(8); C6−C8, 1.385(8). Bottom: structure of the $[C_8S_8]_n^{2n-}$ chains in $(PPh_4)_2C_8S_8$·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 our inability to observe the ^{13}C NMR signals for anything but the PPh_4^+ 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 μ_B per $C_8S_8^{2-}$ 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 $(PPh_4)_2C_8S_8$ occurs at ∼0.0 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 $[C_8S_8]_n$. Electroactive sulfur-rich polymers have attracted recent attention as cathode materials in lithium ion batteries.[19]

Scheme 2[a]



[a] Potentials are vs Ag/AgCl.

Chemical oxidation of DMF solutions of $(PPh_4)_2C_8S_8$ using I_2 ($E_{1/2} \approx 0.34$ V) resulted in immediate precipitation of a orange-brown diamagnetic material (**3**) which analyzes as CS. The IR spectrum of this new form of CS is devoid of bands in the $\nu_{C=S}$ region (∼1100−1000 cm^{-1}), indicating that all four exocyclic sulfur atoms in **3** are involved in S−S bonding. Powder X-ray diffraction analysis shows that this material is crystalline; therefore, we are hopeful of determining its three-dimensional structure. The integrity of the C_8S_8 subunits in **3** was confirmed by reduction of a THF suspension of **3** with 2 equiv of $LiBHEt_3$ to give an emerald green solution from which we could isolate **2** by addition of PPh_4Cl (Scheme 2). Clearly redox-induced polymerization of **2** to give **1** involves only the making and breaking of S−S bonds: the tricyclic core remains intact. Access to THF-soluble $Li_2C_8S_8$ opens the way to an expanded study of this thioanion, e.g., transition metal derivatives.

In summary, well-defined carbon sulfide polymers have been prepared via the stepwise assembly from preformed C_4S_x 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 solvatothermal 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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(16) UV-vis (ϵ): 332 (12 000), 360 (sh), 428 (sh), 442 (42 400), and 596 nm (13 400).

(17) $\Lambda = 110\ \Omega^{-1}\ cm^2\ mol^{-1}$ as measured using a YSI condutivity bridge. The solution conductivity of $(PPh_4)_2[Zn(C_3S_5)_2]$ is 105 $\Omega^{-1}\ cm^2\ mol^{-1}$.

(18) Scan rate 100 mV/s, working electrode Pt, supporting electrolyte 0.1 M NBu_4PF_6.

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