

Photopolymerization of Liquid Carbon Disulfide Produces Nanoscale Polythiencene Films

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Abstract: Broad band solar or 300–400 nm irradiation (Hg–Xe arc source) of liquid-phase carbon disulfide produces a new carbon–sulfur polymer with the approximate ($n = 1.04–1.05$) stoichiometry $(CS)_x$. The polymer, from here on called $(CS)_x$, forms as a ~ 200 nm thick transparent golden membrane as measured by SEM and AFM techniques. IR spectra for this polymer show some similarities with those obtained for the gas-phase photopolymerized $(CS_2)_x$ and the high-pressure-phase polymer of CS_2 , called Bridgman's Black. The observed FT-IR absorptions of $(CS)_x$ include prominent features at 1431 (s, br), 1298 (m), 1250 (ms), and 1070 cm^{-1} (m). In contrast to previous proposals for $(CS_2)_x$, ^{13}C labeling and model compound studies of α -(C_3S_5) R_2 and β -(C_3S_5) R_2 ($R =$ methyl or benzoyl) suggest that the absorption at 1431 cm^{-1} and those at 1298 and 1250 cm^{-1} are indicative of carbon–carbon double bonds and carbon–carbon single bonds, respectively. The molecular structure of α -(C_3S_5)($C(O)C_6H_5$) $_2$, determined at -84 °C, belongs to space group $P\bar{1}$, with $a = 7.486(5)$ Å, $b = 13.335(11)$ Å, $c = 17.830(13)$ Å, $\alpha = 105.60(6)^\circ$, $\beta = 95.32(6)^\circ$, $\gamma = 90.46(6)^\circ$, $Z = 4$, $V = 1706(2)$ Å 3 , $R = 0.0785$, and $R_w = 0.2323$. With use of electron and chemical ionization mass spectrometry, C_4S_6 and C_6S_7 were identified as the dominant soluble molecular side-products derived from a putative ethylenedithione ($S=C=C=S$) precursor. Atomic force microscopy (AFM) provided surface topology information for the thin film $(CS)_x$ and revealed features that suggested the bulk material is formed from small polymer spheres 20–50 nm in size. Both $(CS_2)_x$ and $(CS)_x$ are extensively cross-linked through disulfide linkages and both materials show strong EPR resonances ($g > 2.006$) indicative of sulfur-centered radicals from incomplete cross-linking. A polymerization mechanism based on the intermediacy of $S_2C=C_2S_2$ is proposed.

Introduction

In 1868 Loew published an observation in *Zeitschrift für Chemie* that carbon disulfide yields a brown precipitate when exposed to sunlight.¹ Four years later, a similar finding was published by Sidot who noted that pure CS_2 will “decompose” on exposure to sunlight into sulfur and a maroon-red powder that is odorless and tasteless.² In 1910 one of the first studies was performed on polymeric CS with modern chemical methods. Dewar and Jones found that when $CSCl_2$ is added to $Ni(CO)_4$ a rapid reaction occurs that results in the formation of a brown solid and carbon monoxide.^{3–5} Their conclusions, based primarily on elemental analysis, were that the material was a compound with a one-to-one carbon sulfur ratio, $(CS)_x$, and might be similar to the substance observed by Sidot.²

The most influential findings regarding polymerized CS_2 occurred in 1941, when Bridgman found that if liquid carbon disulfide is heated to 175 °C at 45 kbar in a diamond anvil cell it will slowly change in morphology to a black solid that is stable in air at room temperature. When heated to 200 °C at normal pressure the material decomposes to carbon and sulfur. Bridgman suggested a structure for $(CS_2)_x$ analogous to that of

silicon dioxide.⁶ This finding prompted a series of investigations of the new material, which came to be known as Bridgman's Black carbon disulfide. Subsequent research suggested that this compound contained a mixture of two forms of carbon–sulfur polymers with sulfur–carbon single and double bonds.⁷ New routes to carbon disulfide polymers have attracted recent interest, which include plasma-polymerization, laser-polymerization, sonopolymerization, radiopolymerization, and photopolymerization.^{8–18}

Conjugated sulfur-containing polymers are of interest because of their potential for conductivity, novel magnetic effects, and

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dopability.^{19–27} Polysulfur nitride, for example, is superconductive below 1 K and polythiophene compounds are semiconductors that become conductive after doping.²⁸ Plasma-polymerized carbon disulfide has been used as a cathode material in rechargeable batteries; however, the material made by this process is contaminated with free sulfur.¹³ Because of minimal contamination by free sulfur, CS₂ photopolymers¹⁴ may be viable alternatives to the plasma-polymerization materials.

Photopolymerization of gas-phase CS₂ also provided a novel example of a mass-independent sulfur isotope fractionation,^{15,18} which was similar to those of astrophysical origin.^{29–33} Carbon disulfide is an important component of gaseous nebula and primitive planetary atmospheres. Photopolymerization of CS₂ may represent an important gas-to-particle process in the presolar nebulae.¹⁵ Although gas-phase photopolymerization of ¹³CS₂ yields the (¹³CS₂)_x photopolymer with an anomalously high enrichment in ³³S, ³⁴S, and ³⁶S, liquid-phase photolysis yields solid material of different composition with a normal isotopic signature.¹⁸

The structure of Bridgman's Black carbon disulfide was first probed by Whalley in 1960.³⁴ Using IR spectroscopy, he assigned a strong absorption at 1063 cm⁻¹ to a C=S (thiocarbonyl) stretch, and suggested the simple linear polymer structure $-\text{C}(\text{=S})\text{S}_x-$. Later, Chan and Jonscher proposed a more complicated structure based on a more detailed IR spectrum.⁷ In 1995 the vapor-phase-prepared photopolymers (CS₂)_x and (¹³CS₂)_x were reported.¹⁴ The (CS₂)_x photopolymer exhibits an IR spectrum nearly identical with that for Bridgman's Black. It was concluded that the structure of (CS₂)_x aerosol was similar to the one proposed by Chan and Jonscher for Bridgman's Black, but with thiocarbonyl end groups.

This work describes the characterization of a new carbon-sulfur polymer of approximate stoichiometry (CS)_x, prepared by the photoirradiation of liquid-phase carbon disulfide. Isotopic labeling studies and comparison of IR spectral features with model compounds reveal the presence of C–C, C=C, and S–S bonds in both (CS)_x and (CS₂)_x. Thermochemical arguments favor C–C coupling during the polymerization process and a mechanism for polymer formation based on a S₂C=CS₂ intermediate is proposed.

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Experimental Section

General Methods. All chemicals were used as received unless otherwise specified. THF was freshly distilled from sodium benzophenone ketyl and carbon disulfide was distilled under vacuum from P₂O₅. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, Az.

NMR Experiments. NMR data were collected with 250, 300, or 500 MHz spectrometers and chemical shifts are reported relative to TMS in ¹H spectra and to CHCl₃ (δ 77.0 ppm) in ¹³C spectra. Magic angle spinning (MAS) solid-state ¹³C spectra were acquired at room temperature with a Varian Unity 300-MHz ¹H NMR spectrometer at a sample frequency of 75.426 MHz with a Doty Scientific Inc. probe. Samples (~100 mg, referenced externally to tetrakis(trimethylsilyl)silane at δ 0.0 ppm) were placed in an airtight 7 mm ZrO₂ rotor and spun at 1.5 kHz.

Electron Paramagnetic Resonance (EPR) Measurements. Spectra were recorded with a Bruker ElexSys E500 spectrometer operating at X-band frequency. Temperatures of approximately 6 ± 1 K were obtained with an Oxford helium cryostat. Samples were prepared by placing acetonitrile suspensions of finely divided (CS₂)_x or (CS)_x into quartz EPR tubes and then removing the solvent under vacuum for several hours. Spectral simulations employed the WINEPR SimFonia program from Bruker Instruments.

X-ray Diffraction Studies. Single-crystal X-ray data of all the (C₃S₅) compounds were collected with a Siemens R3m/V four-circle diffractometer using Mo Kα radiation and the low-temperature accessory. Data collection and crystal parameters are only reported for the new isomer α-(C₃S₅)(C(O)C₆H₅)₂ in the Supporting Information. Each of the structures was solved by direct methods (SHELXTL PLUS). All non-hydrogen atoms were refined anisotropically, while the hydrogens were calculated and fixed in idealized positions (*d*(C–H) = 0.96 Å). Tables of positional parameters, bond lengths, bond angles, and anisotropic thermal parameters of the complex cations are available in the Supporting Information. Powder X-ray diffraction measurements were performed with a Scintag XDS-2000. Samples were prepared by placing about 3–5 mg of the finely divided film onto zero background quartz slides.

Vibrational Spectroscopy. IR measurements were taken with the use of a Nicolet 510 FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector that was optimized for the 4000–800 cm⁻¹ spectral region. The sample chamber was purged with N₂ to remove atmospheric CO₂ and H₂O. A Nicolet Magna-IR 550 was used for analyzing the spectral region below 800 cm⁻¹. Samples contained 2–3 mg of dried (CS₂)_x, (CS)_x, or model compound and 150 mg of IR grade KBr, and were ground under nitrogen in an agate mortar and pestle. Finally, the mixture was pressed in a hand-held KBr die assembly. Liquid-phase spectra were measured in CCl₄ solvent. Raman spectroscopy measurements were taken with use of a liquid nitrogen cooled CCD spectrometer (Princeton Instruments Model EUV-1143) and a 10 mW HeNe laser (MWK Industries) tuned to a wavelength of 632.85 nm. The laser was focused onto a powdered sample at a 45° angle from horizontal. Raman light was captured by a simple collector lens attached to a quartz fiber optic cable and transmitted to the CCD. Reflected laser light was removed by a holographic notch filter.

Electron Microscopy. Images were acquired with use of a Cambridge 360 SEM at an accelerating voltage of 200 kV. For (CS₂)_x several 1.8 cm glass disks were placed inside a 2 L quartz Schlenk flask and were coated with the (CS₂)_x aerosol photopolymer that settled out during photolysis. Samples were sputter-coated with gold to a thickness of 300 Å to ensure adequate conductivity. For (CS)_x, a small piece of the thin film photopolymer (~3–4 mm²) was placed, via acetonitrile suspension, on a 1.8 cm glass disk attached to an aluminum mounting post. It was then dried under vacuum for several hours and sputter-coated with gold to a thickness of 300 Å.

Atomic Force Microscopy. Images were obtained with use of a model MMAFM-2 multimode SPM (Digital Instruments, Inc.) in tapping mode. Silicon tips were purchased from Olympic Optical Co. and had a radius of curvature from 5 to 10 nm. They were rated at a resonance frequency of 300 kHz and a spring constant of 42 N/m. Scan

rates between 1.5 and 0.8 Hz were used during image acquisition, and three surface prescans were performed before recording the final image.

Synthesis and Collection of $(CS)_x$. Liquid CS_2 (2–3 mL) was placed in a 250 mL round-bottom Pyrex Schlenk flask and freeze–pump–thaw degassed three times on a vacuum manifold. After the third freeze–pump–thaw sequence, the evacuated flask ($\sim 25 \mu\text{mHg}$ solvent vapor pressure) was placed in direct sunlight. Solar heating promoted refluxing of CS_2 , which coated the walls of the flask with a thin film of liquid. After several hours in the sun, the inside walls of the flask became golden in color, and after 3 days a thin polymer coating had formed. While still in the flask, the film was washed several times with fresh CS_2 , and then dried under vacuum. A small amount of water was added by pipet and allowed to stand for several minutes. During this time, the water wetted the glass forming a layer between the glass and the polymer film. By manually moving the water layer around the flask, the film was detached from the surface. On occasion it was necessary to evacuate the flask for several hours before adding the water and heating to 80–90 °C in a warm water bath to facilitate detachment of the film. When quartz flasks were used instead of Pyrex, the sticking of the polymer film to the surface was especially problematic. Treating the flasks with Me_3SiCl according to the procedure of Cras et al.³⁵ made removal of the polymer film easier. After detaching the polymer film, the water was removed by pipet and acetonitrile was added to suspend the film for removal. Samples were prepared for analysis by heating 20–40 mg of $(CS_2)_x$, or $(CS)_x$, at 100 °C under vacuum for 2–3 h to remove adsorbed acetonitrile, water, and CS_2 . The yield, after 60 h of irradiation in a 250 mL flask, was about 4 mg or 0.24% and limited by the cessation of film growth at 200 nm film thickness. Anal. Found for two determinations: C, 26.08 and 25.39; S, 72.07 and 71.55. Calcd. for $(CS)_x$: C, 27.25; S, 72.72. The analytical data fits a $CS_{1.04-1.05}$ stoichiometry. After the material was heated to 185 °C under vacuum for 3 days a small amount of elemental sulfur sublimed away and the remaining polymer was C (25.74%) and S (70.31), which corresponds to a $CS_{1.02}$ stoichiometry.

Mass Spectrometry. Electron and chemical ionization experiments were performed at the UC Riverside Mass Spectrometry Facility with a VG 7070. Samples for analysis by electron ionization and chemical ionization were prepared by photolysis in the same manner as the synthesis of $(CS)_x$. After several days of solar or UV lamp exposure the flask was placed in a high-frequency sonicator for 10–15 min. After sonication, the carbon disulfide liquid was removed via pipet and placed in a clean sample vial. The liquid was concentrated from an initial volume of 10 mL to about 0.1–0.5 mL under a stream of nitrogen, and then analyzed by gas chromatography–mass spectrometry. In another experiment, this liquid was evaporated to dryness under vacuum and the solid residue remaining was 0.87% carbon and 98.56% sulfur.

Synthesis of $(CS_2)_x$. This vapor-phase-prepared photopolymer was synthesized as described previously.¹⁴

Synthesis of α -(C_3S_5)(CH_3)₂. 4,5-Dimercapto-1,3-dithiole-2-thione [α -(C_3S_5)(CH_3)₂] was prepared according to literature procedures.^{36,37} Crystals for α -(C_3S_5)(CH_3)₂ and β -(C_3S_5)(CH_3)₂ were obtained from THF solution by slow evaporation, mp 99–100 °C {lit.^{36,37} mp 100–101 °C}. ¹H NMR (300.074 MHz, $CDCl_3$) δ 2.49 (s, 6H, CH_3); ¹³C{H} NMR (75.453 MHz, $CDCl_3$) δ 210.57 (S=C), 135.74 (C=C), 19.41 (CH_3).

Synthesis of β -(C_3S_5)(CH_3)₂. 4,5-Dimercapto-1,2-dithiole-3-thione [β -(C_3S_5)(CH_3)₂] was directly synthesized from bis(tetraethylammonium)-bis(1,2-dithiol-3-thion-4,5-dithiolate)-zinc(II), β -[(C_3S_5)₂Zn]-[N(CH₂CH₃)₄]₂, in contrast to the method of Steimeke et al.,²² who obtained the compound from 4,5-bis(benzoylsulfanyl)-1,2-dithiole-2-thione. In our method, 6.00 g of methyl iodide (42 mmol) was added to a 100 mL acetone solution of 7.17 g (10 mmol) of β -[(C_3S_5)₂Zn]-[N(CH₂CH₃)₄]₂ with stirring for 3 h. The solvent was removed in vacuo and 100 mL of THF was added to the remaining yellow solid. The

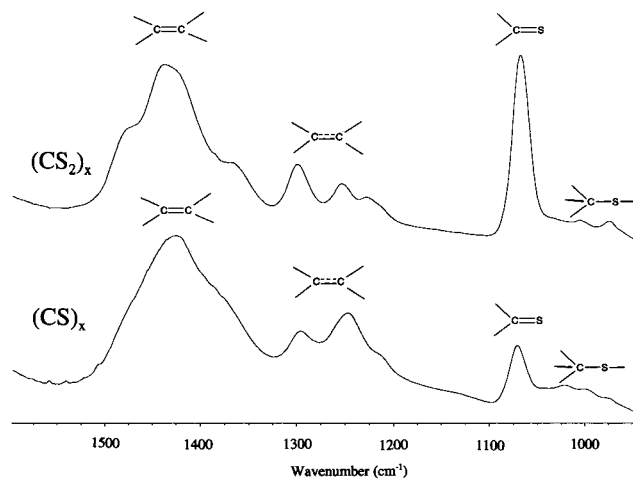


Figure 1. FTIR spectra of $(CS_2)_x$ (top) and $(CS)_x$ (bottom) in a KBr pellet.

yellow solution was filtered off and then concentrated. The yellow crystals of β -(C_3S_5)(CH_3)₂ were obtained in quantitative yield, mp 98–99 °C {lit.³⁶ mp 99 °C}. ¹H NMR (300.074 MHz, $CDCl_3$) δ 2.36 (s, 3H, CH_3), 2.79 (s, 3H, CH_3); ¹³C{H} NMR (75.453 MHz, $CDCl_3$) δ 208.81 (S=C), 134.69 (C=C), 15.89 (CH_3), 15.26 (CH_3).

Synthesis of α -(C_3S_5)(C(O)C₆H₅)₂ and β -(C_3S_5)(C(O)C₆H₅)₂. 4,5-Bis(benzoylsulfanyl)-1,3-dithiole-2-thione and 4,5-bis(benzoylsulfanyl)-1,2-dithiole-2-thione were prepared according to literature routes.^{36,37} Crystals of α -(C_3S_5)(C(O)C₆H₅)₂ and β -(C_3S_5)(C(O)C₆H₅)₂ were obtained from acetone solution by slow evaporation, mp 132–133 °C {lit.³⁷ mp 145–145 °C}. ¹H NMR (300.074 MHz, $CDCl_3$) δ 7.93 (d, 4H, Ph), 7.64 (t, 2H, Ph), 7.48 (t, 4H, Ph); ¹³C{H} NMR (75.453 MHz, $CDCl_3$) δ 211.99 (S=C), 185.10 (C=O), 134.74 (Ph), 134.46 (Ph), 133.39 (C=C), 128.95 (Ph), 127.74 (Ph). Selected data for β -(C_3S_5)(C(O)C₆H₅)₂: mp 170–172 °C {lit.³⁶ mp 171–173 °C}; ¹H NMR (300.074 MHz, $CDCl_3$) δ 8.04 (d, 2H, Ph), 7.94 (d, 2H, Ph), 7.67 (t, 1H, Ph), 7.63 (t, 1H, Ph), 7.49 (t, 4H, Ph); ¹³C{H} NMR (75.453 MHz, $CDCl_3$) δ 209.27 (S=C), 186.93 (C=O), 185.22 (C=O), 169.21 (C=C), 135.77 (Ph), 135.47 (Ph), 134.38 (Ph), 134.35 (Ph), 131.43 (C=C), 129.33 (Ph), 128.93 (Ph), 128.12 (Ph), 128.00 (Ph).

Results

In an attempt to scale-up the gas-phase synthesis of $(CS_2)_x$, an excess of CS_2 liquid was placed in a 2 L quartz reaction flask under vacuum and placed in sunlight. A transparent golden flexible film coated the inside surface of the photolysis vessel walls within several days. Thin surface films were observed previously during the photolysis of liquid CS_2 , but they were not characterized.^{10,14} Although the FT-IR spectrum of the material was very similar to that of $(CS_2)_x$ (Figure 1), its elemental composition approximated that of $(CS)_x$, which corresponds to the unknown but theoretically interesting polymer polythiene.³⁸ Polymer films had been observed previously^{39–42} as side-products from the decomposition of the unstable gas-phase species CS ; however, the chemical-structural nature of these materials was not examined.

Since the photochemical reaction conditions were similar to those of the previous¹⁴ gas-phase synthesis of $(CS_2)_x$, the difference in product composition was attributed to a difference in the phase of the reactant species. The excess, low-boiling

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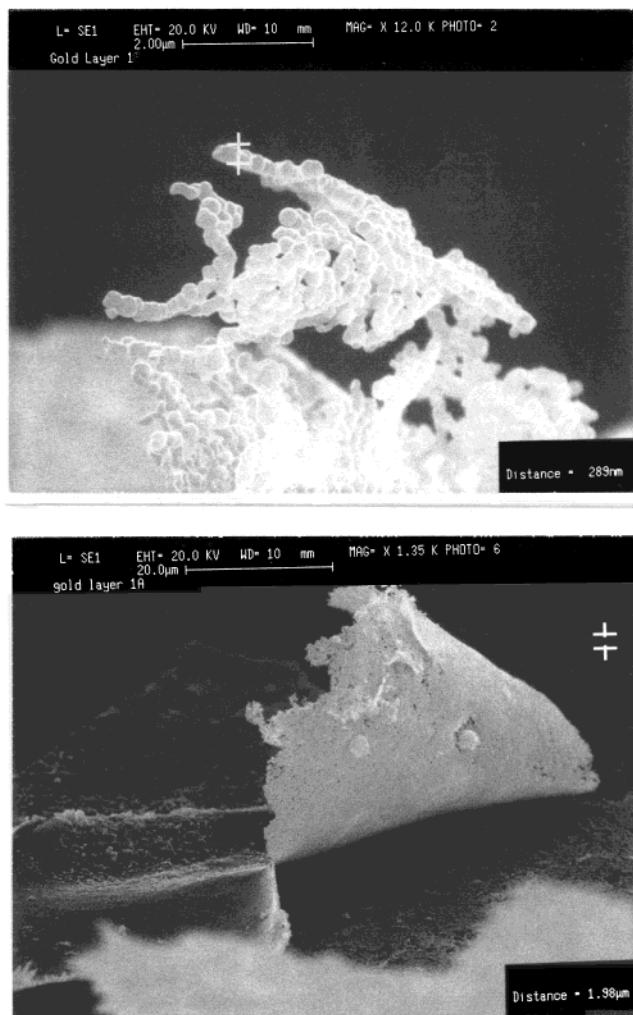


Figure 2. (a) SEM images of $(\text{CS})_x$ synthesized at the liquid-phase carbon disulfide/acetonitrile interface (magnification = 1.35×10^3 times). (b) Increased magnification of Figure 2a (magnification = 12×10^3 times).

CS_2 (bp 46.5 °C) refluxed inside the flask during the solar photochemical synthesis, which raised the possibility that the thin reflux film on the vessel walls was undergoing liquid-phase photochemistry. An experiment was performed in which a 250 mL Schlenk flask was filled with liquid CS_2 , except for a small space covered by black tape to allow for thermal expansion, and placed in direct sunlight. After 3 days, the flask was lined throughout with the golden polymer film except for the small space behind the black tape.

When 100 mL of carbon disulfide and 100 mL of acetonitrile were placed in a 250 mL Schlenk flask an interface formed between the two liquids with CS_2 as the lower layer. After 3 days of solar irradiation, a film had formed between the solvent layers as well as on the walls of the flask adjacent to the CS_2 layer. Elemental analysis showed that the film between the solvent layers had a stoichiometry close to $(\text{CS})_x$, (found: $\text{CS}_{1.08}$). However, it was dull brown in appearance and not as robust as the golden film that formed on the reaction vessel walls. SEM images (Figure 2) of this suggest that it was in the process of forming small particles that had partially joined together, but had not completely fused to a contiguous film. On the basis of the stoichiometry and physical appearance, it is possible that this film undergoes a formation process similar to the wall-deposited film, but at a slower rate. Light attenuation by the acetonitrile and carbon disulfide layers, as well as the

loss of soluble precursor molecules at the interface, may hinder polymer formation.

Both AFM and SEM images support this suggestion. Figure 3 displays an SEM image of the wall-deposited film (at two magnifications) which shows a continuous sheet morphology. Using AFM it was found that this film is made up of particles 20–50 nm in diameter that have joined together resulting in a contiguous layer. On prolonged exposure to the sun, these particles may photoanneal to yield the continuous film. Previous studies of CS_2 photochemistry employed focused light sources, and the small deposits observed when liquid CS_2 was photolyzed were thought to arise from minor surface decomposition.^{6,25} For our studies, the sun was usually used as a light source because of its effectiveness and ease of utilization. The thin polymer film coating the entire reaction flask was readily apparent.

It has already been shown that gaseous carbon disulfide will photopolymerize on irradiation at 313 nm via a long-lived excited state of CS_2 .¹⁶ To investigate the photolysis wavelength dependence for liquid-phase CS_2 , an Oriel Instruments 1000 W He–Xe arc lamp and dichroic mirror were used. In one experiment 10 mL of carbon disulfide was placed in a 500 mL Pyrex Schlenk flask and put inside a box designed to exclude stray UV radiation. Through a small hole in the box, reflected light from the dichroic filter (280–400 nm) was admitted and trained on the center of the flask. The room was kept at an ambient temperature of 30 °C to simulate the summer-time solar irradiation conditions. After 12 h, the polymer film could be seen forming on the inside surface of the flask below the CS_2 liquid level.

An identical sample was exposed to the *unreflected* light from the dichroic mirror ($\lambda < 280$ nm) for the same period of time. In this case, no polymer formed and the liquid was only very slightly yellow in color. Since the Pyrex flask has a cutoff near 270 nm, this latter result serves as an independent test that there is no leakage of higher energy radiation that is actually causing the photochemistry. These experiments conclusively show that the liquid-phase photopolymerization of carbon disulfide requires irradiation wavelengths near its weak 313 nm absorption. Direct photodissociation to CS and S is energetically uphill with 313 nm radiation. It should be noted that besides the weak absorption at 313 nm, which consists of several overlapping $n-\pi^*$ excitations, the next absorption system extends from 230 to 185 nm.¹⁶ The use of Pyrex flasks prevents excitation of the 230–185 nm absorption system, which can cause direct photodissociation.

Using the same experimental conditions, gaseous carbon disulfide (buffered with nitrogen to slightly above atmospheric pressure) in Pyrex flasks was also photoirradiated with the reflected and unreflected light from the dichroic mirror. After 8 h, only the flask that was exposed to reflected 280–400 nm light contained the light brown $(\text{CS}_2)_x$ aerosol photopolymer, which settled slowly.

It is known that $\text{SC}=\text{S}$ double bonds are cleaved at about 102.9 kcal/mol (278 nm).⁴³ To show that formation of the liquid-phase carbon disulfide photoproduct only required 313 nm irradiation, and did not arise from photofragmented CS molecules produced by stray high-energy UV radiation ($\lambda < 280$ nm), liquid CS_2 was irradiated with a 324 nm cut-on filter and dichroic mirror (280–400 nm) to exclude wavelengths below 300 nm. After 2 h the film could be seen forming just as in previous arc lamp and rooftop experiments. Thus, $(\text{CS})_x$ formation does not involve CS precursor derived from direct

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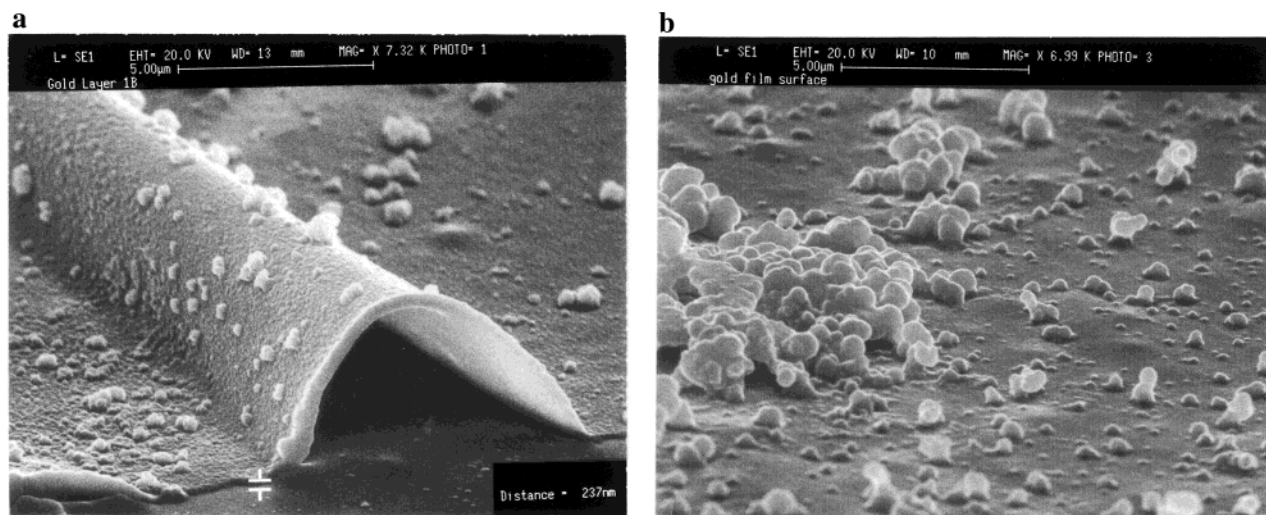


Figure 3. SEM images of $(CS)_x$ at different magnifications: (a) 7.32×10^3 times and (b) 6.99×10^3 times.

photodissociation of CS_2 . An ill-defined decomposition product resulting from direct C–S bond cleavage on irradiation of gas-phase CS_2 at 195 nm has been described previously.¹⁵

For solar irradiation experiments, Pyrex flasks were usually employed and sunlight that reaches the earth's surface contains predominantly long-wave ($\lambda > 290$ nm) UV radiation.²⁹

Characterization. Density measurements of $(CS_2)_x$ and $(CS)_x$ were performed by floating finely divided pieces of each of the polymers in dibromomethane (2.477 g/cm^3)–methanol (0.792 g/cm^3) at 22°C .⁴⁴ Multiple experiments provided the estimated error: $(CS)_x = 1.95 \pm 0.04 \text{ g/cm}^3$. The density of Bridgman's Black carbon disulfide was 1.89 g/cm^3 .⁴⁵ The densities of graphitic carbon and yellow sulfur are 2–2.2 and 1.95 – 2.05 g/cm^3 , respectively.⁴⁶

Neither $(CS)_x$ nor $(CS_2)_x$ dissolved in acetonitrile, acetone, carbon tetrachloride, methanol, dimethyl sulfoxide, *N,N*-dimethylformamide, hexane, petroleum ether, dibromomethane, water, and carbon disulfide. Attempts to force $(CS)_x$ into solution by sonication in acetonitrile and carbon disulfide also failed. Concentrated hydrochloric and sulfuric acids did not attack $(CS)_x$. When placed in concentrated nitric acid or *aqua regia* (HNO_3/HCl), $(CS)_x$ decomposed yielding orange and red-orange solutions, respectively. When placed in a saturated NaOH/isopropyl alcohol solution, the $(CS)_x$ partially deteriorated, but the color of the solution remained unchanged. The lack of solubility of $(CS)_x$ in common laboratory solvents implies that the polymer is highly cross-linked.

Raman spectroscopy and powder X-ray diffraction (XRD) measurements were also employed to investigate $(CS)_x$. The Raman spectrum was dominated by weak fluorescence with no discernible vibrational features. Powder XRD studies indicate that the polymer is amorphous.

FT-IR Spectroscopy. To characterize the IR features common to $(CS)_x$ and $(CS_2)_x$ four model compounds were prepared.^{36,37} The FTIR spectral features of interest for these model compounds are shown in Figure 4. Figure 4a shows the spectrum of 4,5-dimercapto-1,2-dithiole-3-thione. The broad absorptions at 1400 , 1250 , 1225 , and 1050 cm^{-1} from left to right are assigned to the C=C double bond, the C–C single bond (two

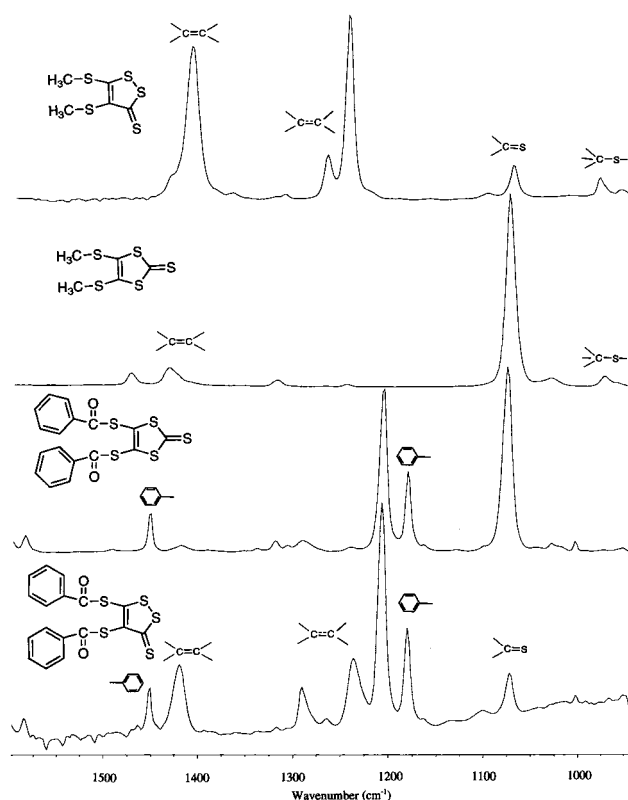


Figure 4. FTIR spectra of carbon–sulfur containing model compounds dispersed in KBr pellets: from top to bottom, (a) $\beta\text{-(C}_3\text{S}_5)(\text{CH}_3)_2$, (b) $\alpha\text{-(C}_3\text{S}_5)(\text{CH}_3)_2$, (c) $\alpha\text{-(C}_3\text{S}_5)(\text{C(O)C}_6\text{H}_5)_2$, and (d) $\beta\text{-(C}_3\text{S}_5)(\text{C(O)C}_6\text{H}_5)_2$.

signals), and the C=S bond stretches, respectively. Figure 4b shows the spectrum of 4,5-dimercapto-1,3-dithiole-2-thione. In this spectrum, the C=C double bond stretch is very weak (due to approximate inversion symmetry of the $S_2C=CS_2$ fragment) and the C=S bond stretch is intense. Previously, the 1400 cm^{-1} absorption was considered to be of too low energy for a C=C double bond stretch.¹⁴ The model compounds show, however, that sulfur-substituted double bonds can exhibit such a low-frequency stretch.

The next two compounds in the series, Figures 4c and 4d, contain additional signals because of the benzoyl moiety, but exhibit similar spectral features. In Figure 4c, 4,5-bis(benzoylsulfanyl)-1,3-dithiole-2-thione, the signal at 1450 cm^{-1} and two signals around 1200 cm^{-1} are due to the benzoyl moieties.

(44) In ref 14, it was incorrectly stated that CBr_4 was used when CH_2Br_2 was actually employed. However, the reported density for $(CS_2)_x$, $1.92 \pm 0.03 \text{ g/cm}^3$, is correct.

(45) Butcher, E. G.; Alsop, M.; Weston, J. A.; Gebbie, H. A. *Nature* **1963**, *199*, 756–758.

(46) Budavari, S. *The Merck Index*, 11th ed.; Budavari, S., Ed.; Merck & Co., Inc.: Rutherford, NJ, 1989.

Otherwise, this spectrum has similar spectral features for C=C, and C=S bonds as Figure 4b. In Figure 4d, 4,5-bis-(benzoylsulfanyl)-1,2-dithiole-2-thione, the C-C bond stretching frequency is shifted to slightly higher energy (1300 cm^{-1}). Again, the C=C stretching vibration is weak when all four atoms bound to the alkene fragment are sulfur atoms. Also, the intensity of the thiocarbonyl stretch is greatly reduced when it is in conjugation with the C=C bond.

The assignment of C-S stretching vibrations is more problematic. These features are of medium to weak intensity and were reported^{36,37} to occur between 470 and 950 cm^{-1} in the model compounds examined. In Figures 4a and 4b weak absorptions near 950 cm^{-1} were assigned to C-S stretching; however, in Figures 4c and 4d the absorptions are of even lower frequency and intensity and are not shown.

The FT-IR spectra of $(\text{CS})_x$ and $(\text{CS}_2)_x$ (Figure 1) exhibit spectral features quite similar to those of the four model compounds. This suggests that the same functional groups that exist in the model compounds also exist in the photopolymers. The polymers' IR absorptions are much broader than the model compounds', which can be attributed to the highly cross-linked nature of the photopolymers and the variety of local chemical environments.

The strong absorption at 1070 cm^{-1} in Figure 1 is characteristic of a thiocarbonyl (C=S) stretch.^{47,48} Samples of $(\text{CS}_2)_x$ have a much larger thiocarbonyl (C=S) stretch at 1070 cm^{-1} than $(\text{CS})_x$. This may reflect a larger number of thiocarbonyl moieties in the $(\text{CS}_2)_x$ photopolymer or conjugation of the thiocarbonyl moieties with carbon-carbon double bonds in $(\text{CS})_x$. Comparing the IR spectra of the α and β small molecule ring compounds, it is observed that in the α -isomers the thiocarbonyl stretches are more intense than in the β -isomers. Conjugation of the thiocarbonyl moiety with the carbon-carbon double bond moiety causes a reduced signal intensity in the β isomers.

In addition to model compound comparisons, the identities of the IR absorptions were established by synthesizing polymers with ^{13}C labeled carbon disulfide (97–99% ^{13}C , Cambridge Isotope Labs). Using a harmonic oscillator approximation, frequency shifts for ^{13}C substituted C=C double bonds and C-C and C-S single bonds were calculated. A ^{13}C substituted C=C double bond at a frequency of 1431 cm^{-1} is predicted to shift to 1375 cm^{-1} .⁴⁹ A shift to 1377 cm^{-1} is observed (Figure 5). Several signals of very weak intensity are observed between 550 and 1000 cm^{-1} . On the basis of the model compounds, this is a region that could contain weak C-S absorptions. The more prominent absorption at 696 cm^{-1} shifts to 679 cm^{-1} in the ^{13}C labeled polymer, which is within 1 cm^{-1} of the shift expected for a C-S stretch.

The two broad absorptions at 1298 and 1250 cm^{-1} are assigned to carbon-carbon single bonds by analogy to the small-molecule IR data. We note that in the α -isomers no carbon-carbon single bond exists, and indeed, no signal is observed in the 1200 – 1300 cm^{-1} range. In the β -isomer, carbon-carbon single bond stretches are observed in this spectral region. The ^{13}C FT-IR data support this assignment. For a C-C single bond, the shift from 1298 and 1250 cm^{-1} is predicted to be 1247 and 1201 cm^{-1} , respectively. A shift to 1248 and 1203 cm^{-1} is observed. Furthermore, the solid-state ^{13}C NMR spectrum shows

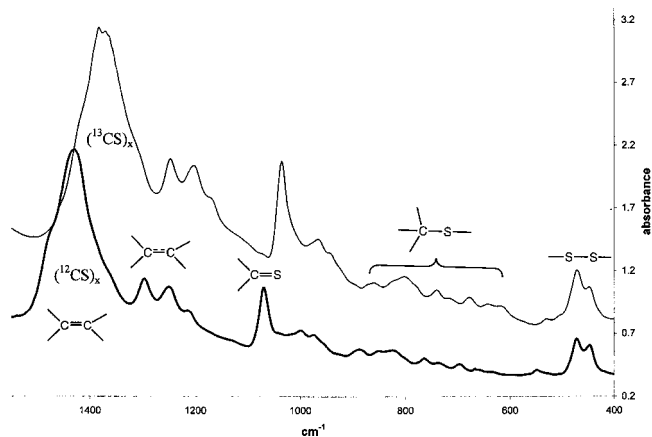


Figure 5. FTIR spectra of $(^{12}\text{CS})_x$ and $(^{13}\text{CS})_x$ dispersed in KBr pellets.

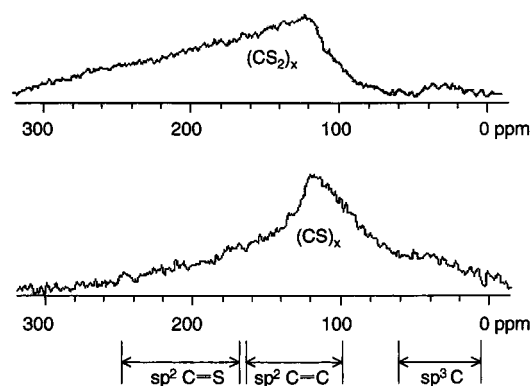


Figure 6. MAS ^{13}C NMR spectra of $(\text{CS})_x$ and $(\text{CS}_2)_x$. Chemical shift ranges for sp^2 and sp^3 moieties are indicated.

no detectable signal in the sp^3 chemical shift region (300 ppm). This suggests that the C-C single bond stretch arises from bonds between the sp^2 hybridized alkene and thiocarbonyl carbons.

Solid-State NMR Measurements. We expected that solid-state NMR measurements would be of limited value because of the highly cross-linked, amorphous nature of the polymer. For materials that are highly cross-linked, solid-state NMR spectra are difficult to interpret since the large number of local environments leads to broad spectral features. In Figure 6, the spectra of $(\text{CS}_2)_x$ and $(\text{CS})_x$ obtained by Magic Angle Spinning ^{13}C NMR (MAS) are shown. The spectral features are very broad, but the chemical shift range was informative. Spin rates of 1.5 and 2.0 kHz were performed and there was no observable change in the broadness of the spectra. The peak that appears at 115 ppm occurs in both spectra and its chemical shift is consistent with the presence of $\text{sp}^2\text{ C}=\text{C}$ double bonds. The shift of the thiocarbonyl carbon's C=S double bonds should appear in the 160 – 240 ppm region, which corresponds to the broad absorption left of the main peak in the $(\text{CS}_2)_x$ spectrum. The relative intensities of this feature in the two spectra support the FT-IR data and suggest that there are more thiocarbonyl moieties in $(\text{CS}_2)_x$ than in $(\text{CS})_x$. Gaussian fits were performed on the spectra to determine the ratio of carbon in C=C and C=S double bonds. In the aerosol photopolymer, $(\text{CS}_2)_x$, the ratio was about $1.0:0.57 \pm 15\%$. In the thin film photopolymer $(\text{CS})_x$ the ratio is about $1.0:0.21 \pm 20\%$.

No signal is detected in the 0 – 60 ppm region, which is characteristic of sp^3 carbons. Thus, the MAS data support the conclusion that C=C double bonds exist in both polymers and that the ratio of thiocarbonyl moieties is greater in $(\text{CS}_2)_x$ than in $(\text{CS})_x$. The broad nature of the NMR absorption is consistent

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(48) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley-Interscience Publications: New York, 1972.

(49) Herzberg, G. *Molecular Spectra and Molecular Structure II*; Van Nostrand Reinhold Ltd.: New York, 1945.

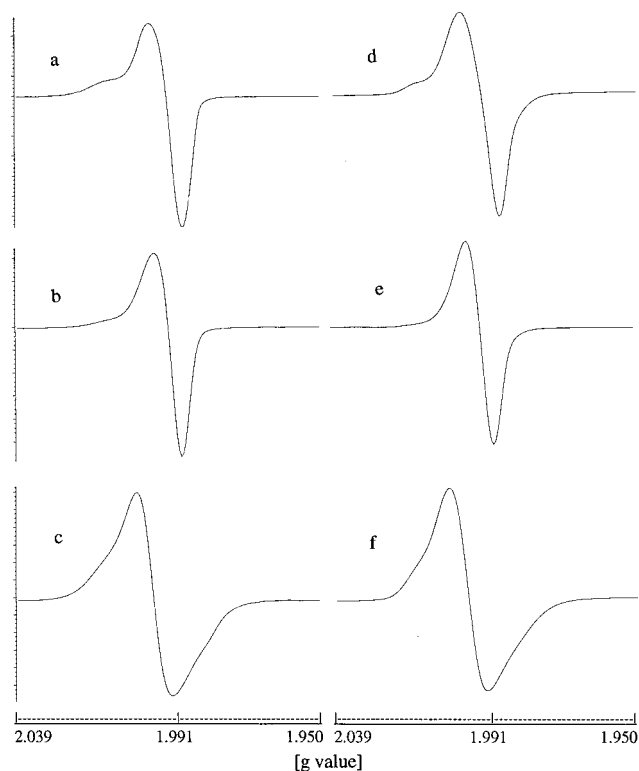


Figure 7. Powder X-band EPR spectra at 6 K of (a) $(CS)_x$, (b) $(CS)_x$ after annealing at 190 °C for 2 days, (c) $(^{13}CS)_x$, (d) $(CS_2)_x$, (e) $(CS_2)_x$ after annealing at 190 °C for 2 days, and (f) $(^{13}CS_2)_x$.

with powder X-ray diffraction data, which indicates that both $(CS_2)_x$ and $(CS)_x$ are amorphous polymers.

EPR Measurements. Because it was postulated that both $(CS)_x$ and $(CS_2)_x$ were extensively cross-linked by disulfide bonds, the EPR spectra were recorded to see whether any dangling $-S^{\bullet}$ radicals were left from incomplete cross-linking. Indeed, both materials showed strong EPR resonances (Figure 7) in the g 2.003–2.007 region. The spectral distribution narrows considerably on annealing at 190 °C, which suggests the presence of several radical environments or weakly interacting species. The spectra of the annealed samples could be fit to a single radical species of effective axial symmetry (for $(CS)_x$ $g_{\perp} = 2.00429$ and $g_{\parallel} = 2.02557$; for $(CS_2)_x$ $g_{\perp} = 2.00509$ and $g_{\parallel} = 2.02783$). Hyperfine splitting to ^{13}C was evident from the significant broadening of the EPR resonances in the ^{13}C enriched materials (Figure 7, spectra c and f), which would correspond to coupling with one or more ^{13}C nuclei with a hyperfine splitting of 10–25 G. Shoulders, which bordered the central absorption resonance of the samples (Figure 7, spectra c and f), are greatly reduced compared to spectra taken at room temperature.

Scanning Electron Microscopy (SEM) Analysis. Studies of the surface morphologies of $(CS)_x$ and $(CS_2)_x$ reveal that $(CS)_x$ is a continuous flexible film that exhibits bends and folds (Figure 3), whereas $(CS_2)_x$ is a loose conglomeration of spherical aerosols. The $(CS)_x$ photopolymer seems to be formed by the aggregation of spherical particles, and on prolonged exposure to sunlight it photoanneals to yield a continuous film. By SEM the approximate thickness of the $(CS)_x$ film was about 200 nm, and the average diameter of the $(CS_2)_x$ aerosols was about 800 nm. The average film thickness of 200 nm for the $(CS)_x$ polymer is reproducible for a wide range of exposure times and irradiation intensities. We infer that film thickness is limited by self-absorption and scattering.

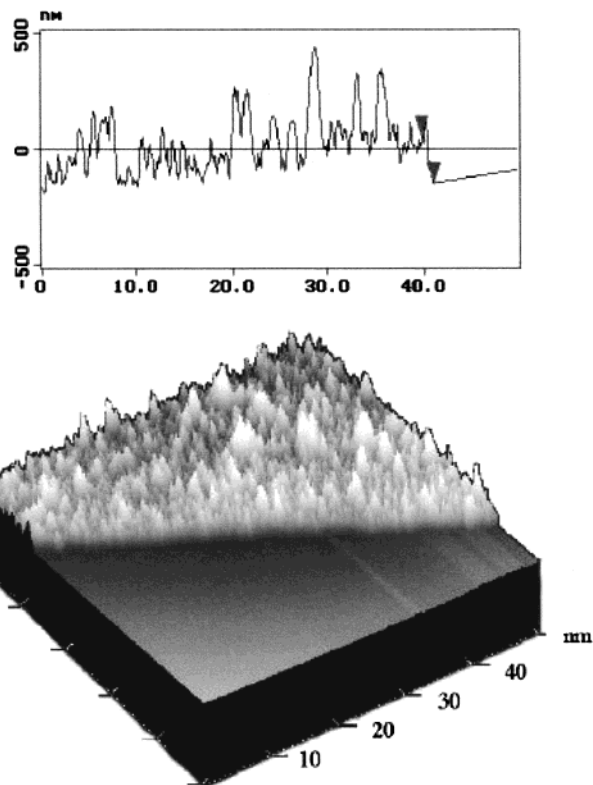


Figure 8. AFM image of the $(CS)_x$ surface. Section analysis between the film and silicon support shows the vertical distance (from triangle tip to triangle tip) is 199.7 nm.

AFM Measurements. AFM images of the $(CS)_x$ polymer revealed an irregular surface topography made up of particles about 20–50 nm in diameter. Cross-sectional analysis shows a variation in surface height features ranging from 10 to 150 nm (Figure 8). By SEM, it appears as if the formation of the polymer occurs from the grouping of particles that ultimately yield a continuous film 200 nm thick. AFM data confirm the SEM thickness measurements. Figure 8 shows an AFM scan across the surface of the polymer and onto the silicon substrate. The approximate difference in height was 200 nm, as observed in the SEM studies.

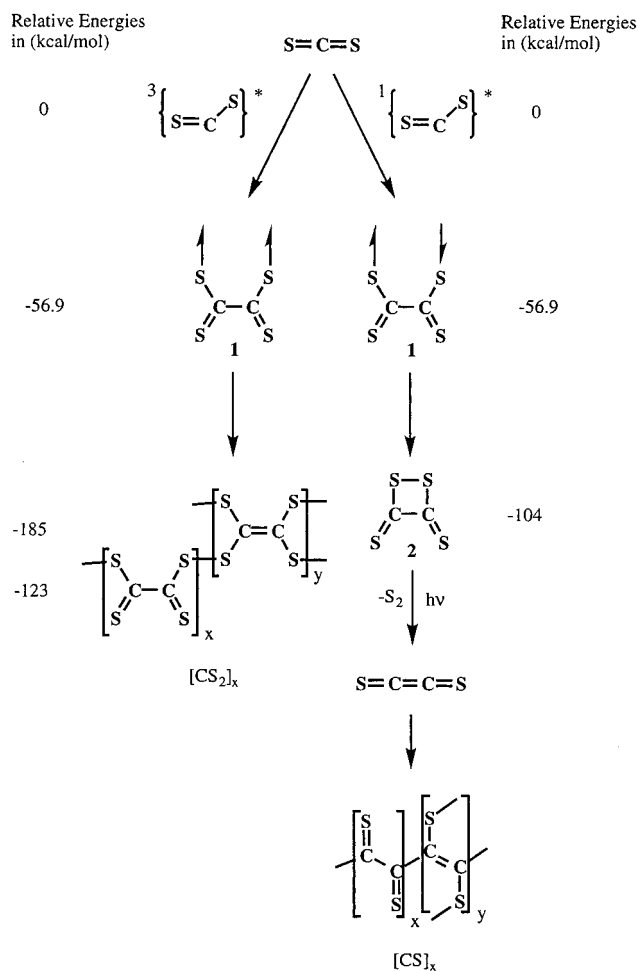
Crystallography. Crystal structures were obtained for the model compounds α - $(C_3S_5)(CH_3)_2$, β - $(C_3S_5)(CH_3)_2$, and α - $(C_3S_5)(C(O)C_6H_5)_2$ to verify their identity. Their structures and melting points matched those previously reported, except for α - $(C_3S_5)(C(O)C_6H_5)_2$. The material crystallized from acetone exhibited a mp of 132–133 °C, which differs from that reported for monoclinic α - $(C_3S_5)(C(O)C_6H_5)_2$ (mp 145–145 °C).^{36,50,51} A single-crystal X-ray determination showed that this resulted from a different crystalline form (triclinic) of α - $(C_3S_5)(C(O)C_6H_5)_2$. The unit cell shows two independent molecules of α - $(C_3S_5)(C(O)C_6H_5)_2$ in the asymmetric unit; however, their metrical parameters are quite similar to that of the monoclinic isomer and are not discussed further.

Mass Spectrometry of Molecular Species Produced during the Formation of $(CS)_x$. Electron ionization (EI) mass spectra consistently showed that elemental sulfur is the primary species dissolved in unreacted carbon disulfide from the photochemical preparation of $(CS)_x$ and that two other carbon–sulfur products are present. These products, found in a 3.05/1 ratio, have

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Scheme 1



molecular weights of m/z 240 and 296. This corresponds to C_4S_6 and C_6S_7 , respectively. Computer modeling of the isotope patterns of C_4S_6 and C_6S_7 match the observed patterns. Chemical ionization (CI) mass spectrometry confirmed that these are parent ions. The solid residue isolated by removal of unreacted carbon disulfide under vacuum consists of 0.87% C and 98.56% S, which corresponds to a mixture of 95.6% S_8 , 2.9% C_4S_6 , and 2.3% C_6S_7 . These and 17 other products were also identified by Heymann et al. They analyzed toluene extracts of carbon-sulfur oligomers generated by broad-band UV irradiation of CS_2 with HPLC, MALDI-TOF, PIXE, and nuclear microprobing.⁵²

Discussion

Because of the highly cross-linked state of the polymer and the lack of average chain length data, it is difficult to suggest a simple bulk phase structure for $(CS)_x$. Nevertheless, experimental data establishes the presence of C=C, C-C, C-S, C=S, and S-S bonds in these materials. Since $SC=S$ double bonds cannot be photolytically cleaved at 313 nm, the reaction most likely proceeds by an excited state addition mechanism. Considering the structural moieties spectroscopically observed and thermochemical estimates (see Supporting Information for detailed values and references), the mechanisms in Scheme 1 are proposed for the initial steps in the formation of $(CS)_x$ and $(CS_2)_x$.

The formation of the carbon-carbon coupled dimer **1**, shown in Scheme 1, is energetically reasonable. Photopolymerization

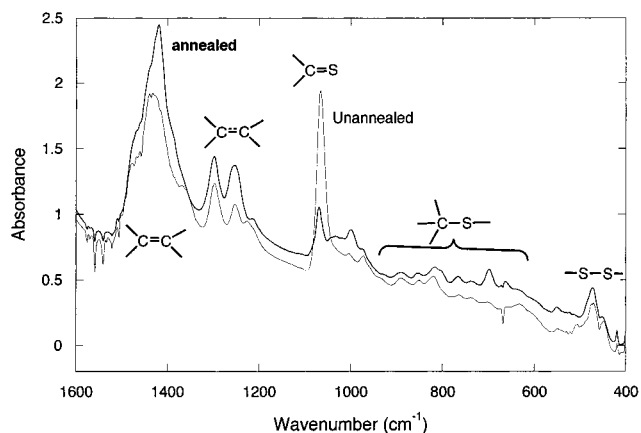


Figure 9. FT-IR spectra of annealed (heavy line) and unannealed (light line) $(CS_2)_x$.

occurs between 300 and 350 nm. Thus, the available excited-state energy is about 95.4 kcal/mol. Since this energy produces the excited-state *CS_2 that reacts with unexcited CS_2 , thermochemical estimates of the reaction need only consider the bonds that are broken and formed (see Supporting Information for values and references). We assume that *CS_2 adopts a bent excited state with single and double carbon-sulfur bonds.⁵³ Therefore, in product **1** a σ C-C bond is made (-85.8 kcal/mol) and a π C-S bond is broken ($+28.9$ kcal/mol). Thus, CS_2 addition to *CS_2 is favored by a reaction energy of about -56.9 kcal/mol, whereas the alternative S-S coupling to produce a $S=C-S-S-C=S$ intermediate is only favored by -37.1 kcal/mol. We propose that the difference between the gas and liquid-phase photolysis products arises because the vapor-phase photochemistry occurs through a long-lived bent triplet excited state of CS_2 to produce triplet **1**. This is suggested by the persistence of the photochemical reaction under conditions where the fluorescence is quenched completely.¹⁷ However, in the liquid phase the high local concentration of CS_2 permits prompt reaction from the initial CS_2 singlet electronic state to form the more stable singlet product **2**. The differing sulfur isotope enrichments observed in the photopolymers prepared by the two methods are also consistent with this hypothesis.¹⁸

In the gas phase, the polymerization reaction is proposed to proceed by S-S coupling of **1** to generate a polymer with two different randomly cross-linked C_2S_4 repeat units as depicted in Scheme 1. Little sulfur is lost as S_8 in the gas-phase reaction and the IR data show the presence of sp^2 carbons, sulfur-sulfur bonds, and carbon-carbon and carbon-sulfur double bonds. In the gas phase, the lower concentration of CS_2 means the probability of collisions resulting in cross-linking is smaller. This produces a high fraction of the $-SC(S)-C(S)S-$ repeat unit, even though the $S_2C=CS_2$ unit (cross-linked by 4 S-S linkages) is thermodynamically favored by about 62 kcal/mol.

Thermolysis studies of $(CS_2)_x$ suggest that the C=S bonds are less stable and thermally reactive. About 4–5 mg of $(CS_2)_x$ was placed under vacuum in a 50 mL Schlenk flask and held at a constant temperature of 185 °C for 5 days. Figure 9 shows the FT-IR spectra of $(CS_2)_x$ and the thermolyzed $(CS_2)_x$. All the signals in $(CS_2)_x$ remain essentially unchanged except for the C=S stretch at 1070 cm^{-1} , which almost disappears. A similar experiment was also performed for $(CS)_x$. Very little change in the IR spectrum was observed.

In the liquid phase, formation of **2** from **1** is spin-allowed since collisional deactivation of the excess excitation energy

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by solvent occurs promptly in the condensed phase and permits bond formation to occur. However, **2** is expected to be susceptible to loss of S₂, which is recovered from the unpolymerized carbon disulfide remaining after photolysis as S₈. Thus, after the initial loss of sulfur from **2** to yield the carbon suboxide analogue, ethylenedithione,⁵⁴ it polymerizes to produce (CS)_x. Cross-linking in the polymer appears to be more extensive than for (CS₂)_x, as evidenced by the reduced relative intensity of the thiocarbonyl stretch in the IR spectrum. However, conjugation between the C=S and C=C bonds in the polymer (Scheme 1) could also contribute to the reduced intensity. Species **2** has recently been suggested as an energetically reasonable intermediate for the polymerization of carbon disulfide based on density functional theory calculations.⁵⁵

EI and CI mass spectrometry studies of the unreacted CS₂ solution remaining after photolysis identified C₄S₆ and C₆S₇ as minor byproducts. These compounds may be the result of a side reaction between C₂S₂ and CS₂. An additional small signal was observed at *m/z* 296, which could result from the dimerization of a C₃S₄ intermediate to produce the known compound C₆S₈.⁵⁶ Loss of sulfur would then produce C₆S₇. Direct addition of C₂S₂ to **1** would be another potential pathway to yield another isomer with a C₄S₆ stoichiometry.

The polymer shown in Scheme 1 contains all the structural moieties that were found spectroscopically in the condensed-phase carbon disulfide photopolymer. It was shown by MAS NMR, FT-IR spectroscopy, and elemental analysis that the ratio of carbon in C=C double bonds vs C=S double bonds is about 1.0:0.21 and that the overall ratio of sulfur to carbon was slightly greater in sulfur (CS_{1.04–1.05}). Incorporation of small amounts of **1** into the (CS)_x polymer structure could account for the slight excess sulfur stoichiometry. The C=C to C=S ratio implies that additional cross linking may be occurring thereby reducing the number of thiocarbonyl groups in the system.

EPR results for both materials (Figure 7) show a surprisingly broad complex (*g* = 1.996–2.02) resonance indicative of several radical species. Thiyl radicals have been observed at *g* values as high as 2.0133 to 2.28,^{57–59} and polysulfur radicals found in molten sulfur, amine solvents, and oleum exhibit *g* values

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(59) Balagopalakrishna, C.; Abugo, O. O.; Horsky, J.; Manoharan, P. T.; Nagababu, E.; Rifkind, J. M. *Biochemistry* **1998**, *37*, 13194–13202.

between 2.003 and 2.039.⁶⁰ Although annealing at 185 °C reduced the breadth of the resonance, the remaining EPR line shape exhibited anisotropy either indicative of a single anisotropic thiyl radical or overlapping contributions from more than one type of radical center. Since the cross-linking model (Scheme 1) proposed requires that radical species generated from broken disulfide bonds be in close proximity, this raises the possibility of spin–spin interactions as an additional source of broadening.⁶¹ Presumably the breadth of this resonance reflects the distribution of distances and exchange coupling between proximate radicals, as well as the contribution of isolated thiyl radical centers with different local environments. It is also possible that the lower *g* component arises from some polysulfur radicals trapped in the material. Both (CS₂)_x and (CS)_x contain small amounts of extractable sulfur as initially prepared. The sharpening of the resonance on annealing suggests that some of the more reactive proximate radicals may form a bonded pair during annealing. Broadening of the resonance in the ¹³C labeled material is consistent with the predominant sulfur radical centers being bound carbons as required by the model of Scheme 1.

Acknowledgment. We thank Charles Gram for assistance with the SEM measurements, Boyce Collins for help obtaining the AFM measurements, Roger Isaacson for assistance with EPR measurements, and Robert West and Jarrod J. Buffy for the MAS NMR spectra. The National Science Foundation (Grant No. CHE-9632311) is acknowledged for financial support of this research.

Supporting Information Available: Tables giving details of the thermochemical estimates, X-ray crystallographic data, atomic coordinates and isotopic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for α-(C₃S₅)(C(O)C₆H₅)₂ and figures depicting the two independent α-(C₃S₅)(C(O)C₆H₅)₂ molecules in the triclinic unit cell, the AFM oblique angle image of (CS)_x showing 20–50 nm dimension surface features, the SEM images of (CS₂)_x at 977 times and 5 × 10³ times magnification, and the electron ionization mass spectra of the CS₂ soluble species remaining after a photoirradiation experiment (peaks at *m/z* 128, 160, 192, 224, and 256 correspond to S₄, S₅, S₆, S₇, and S₈, respectively, and peaks at *m/z* 240 and 296 correspond to C₄S₆ and C₆S₇, respectively) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA003200J

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