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The Structure and Properties of Poly[Carbon Dichalcogenides]

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THE STRUCTURE AND PROPERTIES OF POLY(CARBON DICHALCOGENIDES)

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ABSTRACT

The structure and properties of various reaction products resulting from the polymerization of carbon disulfide and carbon diselenide are reviewed. In many respect, CSe_2 behaves like CS_2. However, CS_2 can be polymerized (without a catalyst and in the absence of irradiation) only under high pressure, and this reaction yields a semiconductor. On the other hand, CSe_2 is easily polymerized under ambient conditions. Depending upon the polymerization conditions, products are obtained which range from insulators to metals and superconductors. Results indicate that (CSe_2) reacts to form a head-to-head linear polymer, which thermally decomposes at relatively low temperatures to produce free selenium. This free selenium is the likely origin of the observed superconductivity.

INTRODUCTION

Delocalized chalcogen-based polymers are of special interest because of the observation of superconductivity in polymers such as $(SN)_n$ [1, 2], brominated $(SN)_n$ [1], and $(Se)_n$ [3], as well as in chalcogenide-containing charge-

transfer complexes [4-7], where interchalcogenide interactions are believed to be important for stabilizing the superconducting state. However, little is known about the structures and properties of these polymers. Thus, as part of our interest in electroresponsive organic polymers, we have initiated a detailed investigation of poly(carbon dichalcogenides). We here review present progress.

RESULTS AND DISCUSSION

Poly(Carbon Diselenide)

(CSe$_2$)$_n$ Prepared under High Pressure

Carbon diselenide (CSe$_2$) polymerizes at the rate of about 1 wt% per month at room temperature and atmospheric pressure [8, 9]. The solid obtained was reported to be a linear polymer.

In 1982, one of the authors reported that a solution of CSe$_2$ (dissolved in organic solvents such as methylene chloride and dioxane) polymerizes readily under high pressure (~5 kbar) at ~100°C (Method 1). The product is electrically insulating and amorphous. When this insulator was heated under nitrogen atmosphere at 130-160°C, it converted to a stable black material which was found to have a room-temperature conductivity of 10^{-3} S/cm [10]. Kobayashi and coworkers [11-14] varied the synthetic method of Okamoto and Wojciechowski by eliminating the solvent. They showed that neat CSe$_2$ polymerizes under high pressure (~5 kbar) at 100°C (Method 2). This product was subsequently annealed at ~130°C under reduced pressure to yield a highly crystalline and conductive product with a room temperature conductivity of ~50 S/cm. In addition to the highly conducting crystalline product, amorphous semiconducting and insulating samples of reacted CSe$_2$ can be prepared by varying the reaction conditions and annealing temperature [11-13]. They proposed a two-dimensional structural model for the conductive product, which is shown in Fig. 1.

With the aim of understanding the structure and properties of these novel compositions, we have prepared samples using the synthetic route reported by Kobayashi et al. [11-13]. These samples have a room-temperature conductivity of 10-20 S/cm and a powder x-ray diffraction pattern that is essentially the same as that reported by Kobayashi et al. [11].

Although the (CSe$_2$)$_n$ prepared in organic solvent under pressure (Method 1) was found to be essentially amorphous by x-ray diffraction, the product obtained from neat CSe$_2$ under high pressure (Method 2) was crystalline. The
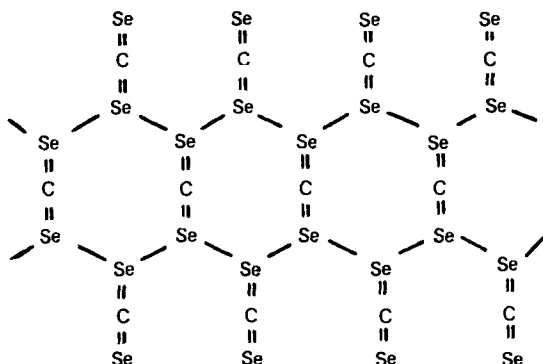
```
        Se          Se          Se          Se
        ‖           ‖           ‖           ‖
        C           C           C           C
        ‖           ‖           ‖           ‖
  ╲   ╱ Se ╲   ╱   Se ╲   ╱   Se ╲   ╱   Se ╲
     Se          Se          Se          Se
     ‖           ‖           ‖           ‖
     C           C           C           C
     ‖           ‖           ‖           ‖
  ╱ Se ╲   ╱   Se ╲   ╱   Se ╲   ╱   Se ╲   ╱
        Se          Se          Se          Se
        ‖           ‖           ‖           ‖
        C           C           C           C
        ‖           ‖           ‖           ‖
        Se          Se          Se          Se
```

FIG. 1. The two-dimensional structure model for conductive poly(CSe_2) proposed by Kobayashi et al. [13].

x-ray diffraction pattern of the $(CSe_2)_n$ is shown in Fig. 2, together with a schematic pattern for trigonal Se [15].

Except for an extremely weak line with a d-spacing of 3.37 Å reported by Kobayashi et al. [13], the spacings and relative intensities of the lines in Fig. 2 essentially correspond to those reported by these authors and assigned to a $(CSe_2)_n$ polymer. It is evident from Fig. 2 that the crystalline component in samples of reacted CSe_2 is not due to a $(CSe_2)_n$ polymer, but is instead due to trigonal Se [16].

Differential scanning calorimetry (DSC) thermograms for the initial heating scan ($20°C/min$) of the reaction products prepared by Methods 1 and 2 are shown in Figs. 3(a) and 3(b), respectively. The Method 2 product shows two melting endotherms, a broad peak at $183°C$ and a narrower peak at $223°C$. These transitions are unambiguously assigned, respectively, to the melting of small-crystallite-size and large-crystallite-size selenium. This assignment is based on diffraction studies through the melting range, as well as a calculation of the effect of crystallite size on melting temperature [16]. By contrast, the initial heat-up of a reaction product obtained by Method 1 (Fig. 3a) shows a broad exothermic peak between about 130 and $240°C$, which is assigned to polymer degradation. Superimposed on this broad exotherm are endothermic peaks (at ~160 and ~$190°C$, uncorrected for shifts due to the superimposed exothermic peak), which we assign to the melting of small-crystallite-size and large-crystallite-size trigonal selenium, respectively, which result from thermal decomposition.

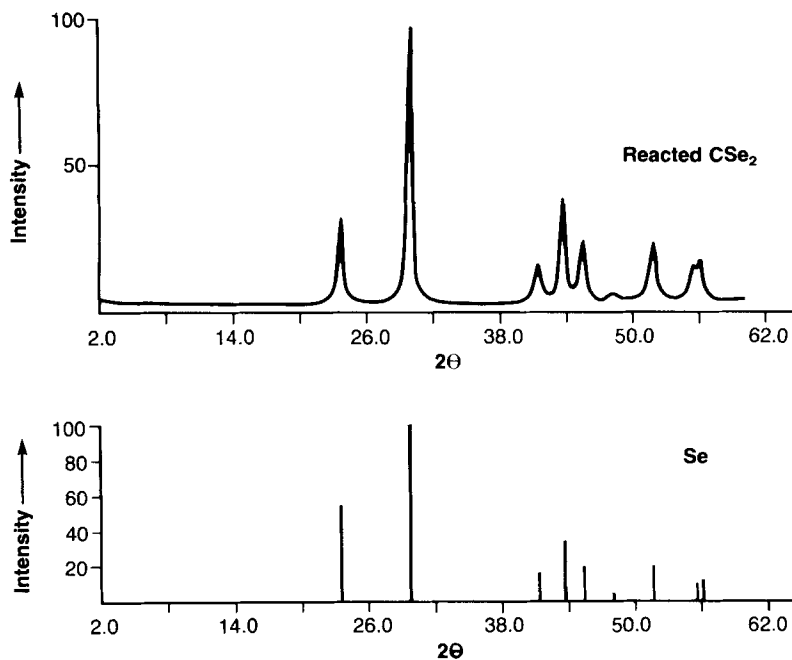This assignment is obtained from 1) the absence of the x-ray diffraction

FIG. 2. X-ray diffraction pattern for a sample of $(CSe_2)_n$, together with the schematic powder pattern of trigonal Se.

peaks due to trigonal selenium in the as-prepared Method 1 product and the presence of these peaks after thermal annealing at 175°C (2 h in vacuum), and 2) the diffraction studies and thermal analysis [16] which provided the assignment of melting endotherms for the Method 2 product. It is reasonable to speculate, using these results, that thermal degradation of Method 1 poly(carbon diselenide) at temperatures much lower than the equilibrium melting temperature of trigonal selenium results in small-crystallite-size selenium and higher temperature degradation results in larger-crystallite-size selenium. The total enthalpy of the degradation exotherm, including the endothermic contributions from the melting transitions, is 52 cal/g. This is a large energy compared with the 18.9 cal/g melting enthalpy of trigonal selenium.

Note that heat released during polymerization and polymer degradation might result in the observed differences in the reaction products obtained by thermal polymerization of neat CSe_2 and CSe_2 solutions at the same pressure
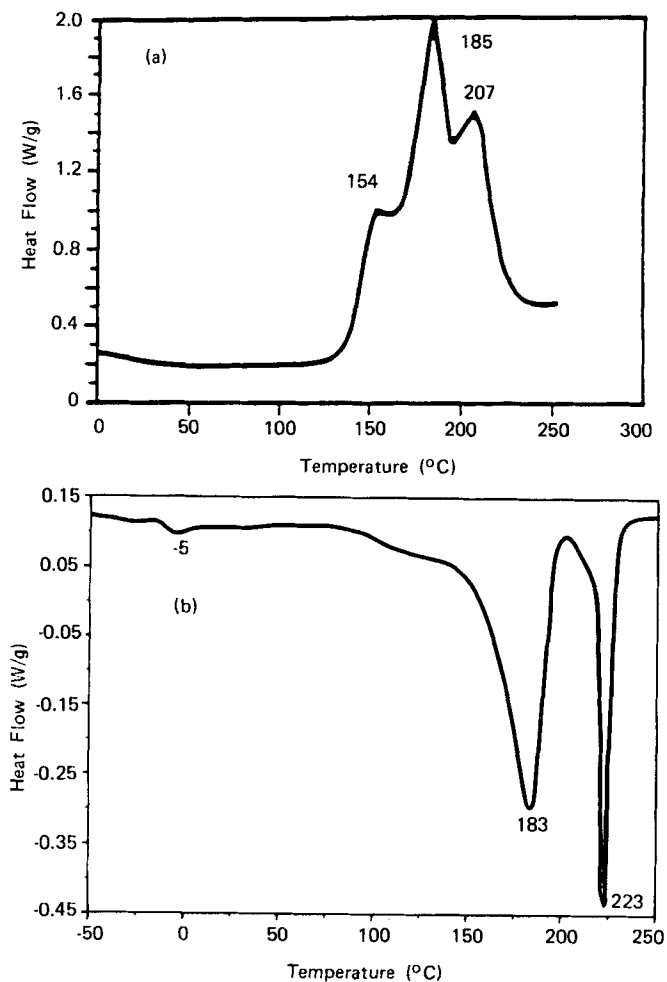
FIG. 3. Differential scanning calorimetry of $(CSe_2)_{\underline{n}}$ $(CSe_2)_{\underline{n}}$ prepared by Method 1 (a) and by Method 2 (b).

and the same nominal temperature (temperature of the external surface of the piston-cylinder pressure cell, which is the temperature referred to in the descriptions of synthesis methods). As a consequence of this heat released by reaction, the temperature of the cell contents can exceed the nominal temperature. This temperature enhancement effect is expected to be largest

TABLE 1. Chemical Analysis of the CS_2-Extracted Samples

Sample	Found[a]		Calculated formula
	C, %	Se, %	
II	10.40	89.60	$CSe_{1.31}$
III	9.48	90.65	$CSe_{1.45}$
IV[b]	12.89	89.93	$CSe_{1.04}$
V	13.36	86.98	$CSe_{1.00}$
VI[b]	11.12	89.02	$CSe_{1.20}$

[a]Calculated value for CSe_2: C = 6.98 and Se = 93.02%.
[b]Samples were ground to a fine powder and extracted with CS_2 for 4 d.

for the reaction of neat CSe_2, which could explain the common observation of free selenium in the reaction product from neat CSe_2 (but not in the reaction product of CSe_2 solutions).

Since trigonal selenium has some solubility in CS_2, the product obtained by Method 2 was extracted with CS_2 with a Soxhlet apparatus for 2 to 4 d. Typical chemical analyses of the extracted samples are summarized in Table 1. The ratio of carbon to selenium after the extraction approximately approaches a nominal 1:1 composition.

The DSC data for the CS_2-extracted sample show that the free trigonal selenium melting at 220°C is greatly reduced after extraction. However, the amount of selenium corresponding to the melting endotherm around 180°C is found to remain unchanged.

Transmission electron microscopy of microtomed sections of unextracted $(CSe_2)_n$ prepared by Method 2 showed that the product consisted of two domains of free selenium crystallites: one domain consisting of 150-250 Å crystallites and the other consisting of about 20 Å crystallites. The larger selenium crystallites can be extracted with CS_2. However, the smaller crystallites appear to be dispersed in a matrix of the amorphous polymeric phase and, hence, cannot be extracted with CS_2.

Assuming the correctness of the above assignments, the total heat of fusion of the free crystalline Se can be evaluated from the DSC data. This heat of fusion is normalized with respect to the total selenium content in the samples as determined by chemical analysis. On comparing these values for the samples prepared by Method 2 with that of pure Se, we find that the total heat

of melting, involving both large (mp 220°C) and small (mp 180°C) crystallites, is about 27% lower than the value for pure Se. Thus, a mole of reacted CSe_2 consists of about 1.5 mole of free selenium and 1 mole of a carbonaceous phase having the approximate composition $CSe_{0.5}$.

Extended x-ray absorption fine structure (EXAFS) spectroscopy of the $(CSe_2)_n$ prepared by Methods 1 and 2 and for the model compounds, trigonal Se and diphenyl diselenide was conducted [18]. The results show the presence of a Se–Se bond in the product prepared by Method 1, with a bond distance (2.32 Å) that is comparable to that for trigonal Se (2.37 Å). The coordination number of selenium bonded to selenium ($N = 0.8$) approaches that of diphenyl diselenide ($N = 1.0$), indicating that Se chains cannot explain the results. The observed carbon-selenium bond distance (1.94 Å) is similar to that of diphenyl diselenide (1.93 Å), and the number of carbons bonded to selenium (0.6) deviates from unity by an amount that is small enough to be due to uncertainties in the determination.

The ESR spectrum at 23°C for the $(CSe_2)_n$ prepared by Method 1 has a broad signal at $g = 2.26$ with a peak-to-peak width of 480 G. The weaker signal at $g = 2.024$, with some structure, is superimposed on the broad line. The high g-value of the broad peak, relative to the free electron value of 2.0034, suggests that this signal is associated with radicals centered on the selenium rather than the carbon atom.
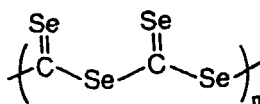
The peak frequencies of the infrared and Raman lines of the $(CSe_2)_n$ obtained by Method 1 are listed in Table 2, together with probable assignments. These data suggest that the product is a highly disordered carbon diselenide polymer containing –C–C–, –C̈=Se, and –C–Se–Se–C– units.

The four-probe dc conductivity of compacted samples of extracted and unextracted $(CSe_2)_n$ prepared by Method 2 was measured as a function of temperature down to 8 K. The room-temperature conductivity (σ_{RT}) for the extracted and unextracted samples is 11.0 and 9.0 S/cm, respectively, consistent with the partial removal of the semiconducting selenium phase on extraction. The ratio σ_{RT}/σ_{8K} is 2.5 for both samples, indicating that the compacted products show metallic behavior.

Based on these results, it appears that the Method 1 polymer is head-to-head poly(carbon diselenide), I, rather than the head-to-tail polymer, I'.
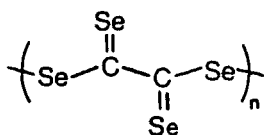
I. Head-to-head polymer of CSe_2

I'. Head-to-tail polymer of CSe_2

TABLE 2. Infrared and Raman Peak Frequencies (in cm^{-1}) and Relative
Intensities for $(CSe_2)_n$ Obtained by Method 1, Together with Probable
Assignments[a]

IR	Raman	Assignment
1410 m	1475 s 1400 s	C=C stretch, polymer
1355 m 1325 m		
1265 s	1236	CSe_2—monomer, ν_3
950 w		
895 s 865 s		C=Se stretch, polymer
730 m[b]		
360 m		CSe_2—monomer, ν_1
300 m		CSe_2—monomer, ν_2
	290 w	C–Se stretch, polymer
	240 m	Se–Se stretch, polymer

[a]Qualitative peak intensities: s = strong, m = medium, w = weak.
[b]This line is believed to be due to an impurity or a reaction by-product.

This is consistent with thermodynamic calculations that predict a lower energy
for I than for I′ [19]. Thermal decomposition of the Method 1 product results
in the formation of free selenium, which is found in the as-prepared Method 2
product. The superconductivity of the product prepared by Method 2 is now
believed to result from the free selenium in this material.

It is interesting to note that carbon selenosulfide (CSeS) dissolved in methyl-
ene chloride or dioxane does not react under reaction conditions (6 kbar and
120°C for 10 h) similar to those used to polymerize CSe_2 [10]. Also, when
CSe_2 was mixed with a large excess of CS_2 and polymerized under these condi-
tions, only a selenium-containing reaction product resulted. This product was
identified to be the same as that produced by Method 1.

Anionic Polymerization of CSe_2

Jensen and Neilsen [20] reported that tripropylphosphine reacted with CSe_2 in ether and yielded a complex having the composition $(C_3H_7)_3P(CSe_2)_4$. They postulated that the structure corresponded to the following oligomer of CSe_2:

$$R_3P^+-\underset{\underset{Se}{\|}}{C}-Se-(\underset{\underset{Se}{\|}}{C}-Se)_2-\underset{\underset{Se}{\|}}{C}-Se^-$$
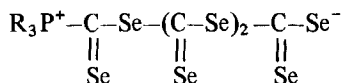
We attempted to polymerize CSe_2 with various anionic initiators such as C_4H_9Li, amines, Na-DMSO, and PR_3. However, the resulting products were dark brown mixtures that could not be purified (see section on the anionic polymerization of CS_2).

$(CSe_2)_n$ Prepared at Ambient Pressure by Thermal and Photo-Induced Polymerization of CSe_2

A black polymeric material was slowly formed by the reaction of neat CSe_2 at 1 atm and 25°C. The electrical conductivity was below 10^{-6} S/cm, which is consistent with a band gap of ~ 2 eV obtained by diffuse reflection spectroscopy [18]. The similarity in Raman and infrared spectra of this product and the product of Method I [head-to-head $(CSe_2)_n$] indicates that the product is also the head-to-head polymer I instead of the head-to-tail polymer I' (which is contrary to previous [8, 9] conclusions).

Upon ultraviolet irradiation (5-15 min exposure to a 1000-W low-pressure Hg lamp emitting primarily at 257.9 nm) of the 5-10% solution of CSe_2 in methylene chloride at 1 atm and 22°C, a golden brown, optical-quality thin film (~ 500 nm thick) was deposited on the inside surface of a quartz cuvette containing the CSe_2 solution. The Raman spectrum of this film is essentially identical to that of the Method 1 polymer.

Poly(Carbon Dilsufide) $(CSe_2)_n$

$(CS_2)_n$ Prepared under High Pressure

Bridgman first showed that CS_2 can be polymerized under high pressure (>45 kbar) at around 175°C and obtained as a black solid with semiconducting properties [21]. Whalley later measured the IR spectra of $(CS_2)_n$ synthe-

sized under high pressure and assigned a head-to-tail linear polymeric structure
[22]:

$$
\begin{array}{cc}
\text{S} & \text{S} \\
\| & \| \\
-\text{S}-(\text{C}-\text{S})_n-\text{C}- &
\end{array}
$$
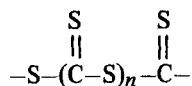
On the other hand, Chan and Jonsher [23] investigated in detail the polymer-
ization of CS_2 under high pressure. They reported that the products were
varied depending upon the experimental conditions. They isolated two prod-
ucts; a low-conductivity material ($<10^{-13}$ S/cm) and a semiconductive mate-
rial (10^{-3} S/cm). The latter product was found to be a mixture of free sulfur
and a C–S polymer. The structure for the $(CS_2)_n$ obtained under high pres-
sure without formation of free sulfur was proposed [23] to be the crosslinked
polymer, as shown in Fig. 4.

However, the experimental results suggest that the polymerization of CS_2
might be similar to that of CSe_2, discussed above. Our thermodynamic calcu-
lations indicated that the head-to-head poly(carbon disulfide) structure is
3.9 kcal/mol lower in energy than the head-to-tail structure [19]. Thus, the
polymerization of CS_2 under high pressure might initially yield the head-to-
head polymer. Depending upon reaction conditions, this polymer might de-
compose into free sulfur and a carbonaceous sulfur-containing polymer simi-
lar to that obtained upon thermal degradation of the head-to-head poly(car-
bon diselenide). However, the calculated preference for head-to-head
poly(carbon disulfide) is much less than that calculated for poly(carbon di-
selenide (19 kcal/mol) [20]. Also, detailed structural data excluding either
the head-to-tail or the head-to-head structure are not available for poly(car-
bon disulfide). Hence, differentiation between these structures for poly(car-
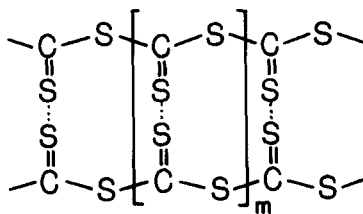bon disulfide) is not presently possible.

FIG. 4.   Crosslinked $(CS_2)_n$.

Anionic Polymerization of CS_2

Recently Tsukamoto and Takahashi [24] reported that CS_2 had been polymerized with Na dispersed in dimethylsulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) at $10°C$. The resulting polymer had the composition $(CS_{1.9})_n$ from the elemental analysis results, and the conductivity was found to be 10^{-8} S/cm but increased to between 10^{-2} and 10^{-3} S/cm with ammonia and iodine doping [24]. They suggested that the structure was close to that of the crosslinked polymer (Fig. 4).

We repeated the polymerization of CS_2 using Na-DMSO and Na-NMP as the initiator and obtained black solids whose compositions were found to vary depending upon the reaction conditions and purification procedure. We obtained a solid product having a composition of CS_m, where $m = 1$-1.8, and spectroscopic data showed that this material is a mixture of various reaction products.

$(CS_2)_n$ Prepared by Miscellaneous Methods

Photolysis [25], plasmalysis [26, 27], or irradiation [28] of CS_2 were reported to yield light brown to black polymers. The structures have been described [16] as $(C_3S_2)_n$, $(CS(S)_m)_n$, or mixtures thereof for the products obtained in photolysis or plasmalysis. It is now well established that CS is produced as a reaction intermediate of both photolysis and plasmalysis. It appears that CS reacts to yield a variety of products, depending upon reaction conditions.

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