

## Reaction of Carbon Diselenide under High Pressure: Synthesis and Characterization of Poly(carbon diselenide)

Yoshiyuki Okamoto\* and P. S. Wojciechowski

Department of Chemistry, Polytechnic Institute of New York, 333 Jay Street, Brooklyn, New York 11201, U.S.A.

A new type of reaction of  $\text{CSe}_2$  under high pressure and a new method for the preparation of poly(carbon diselenide) are reported; the polymer is highly conducting and stable up to  $300^\circ\text{C}$  and in air.

In many respects carbon diselenide behaves like carbon disulphide. However, carbon disulphide can be polymerized only under high pressure and at high temperature, *e.g.*, 45 000 atm at over  $175^\circ\text{C}$ . On the other hand, carbon diselenide polymerizes readily. Carbon diselenide was reported to yield a black solid at the rate of about 1% per month at room temperature<sup>1,2</sup> and atmospheric pressure. The solid obtained was reported to have a linear polymeric structure (1) which is similar to poly(carbon disulphide).<sup>2</sup>

We have found that when  $\text{CSe}_2$  in methylene chloride or dioxan was pressurized at about 5000 atm and heated at  $100^\circ\text{C}$  for 20 h, a black solid was obtained in 95% yield. The solid was not soluble in common organic solvents. After the solid was dried under reduced pressure at  $80\text{--}90^\circ\text{C}$  for several hours, the i.r. spectrum was taken of a dispersion in KBr. There is a strong band at  $880\text{ cm}^{-1}$  which was assigned to the  $\text{C=Se}$  stretching vibration.<sup>2</sup> In addition, there are absorptions at 1260 and  $1380\text{ cm}^{-1}$ . The  $1260\text{ cm}^{-1}$  band was due to the asymmetric stretching of  $\text{CSe}_2$ .<sup>3</sup> When the solid was heated under reduced pressure, it appeared to decompose at *ca.*  $160^\circ\text{C}$ . However, the thermogravimetric study of the solid showed that only several percent of the weight was lost at *ca.*  $160^\circ\text{C}$  and the solid remaining was stable up to  $300^\circ\text{C}$ . The weight lost at  $160^\circ\text{C}$  was variable and depended upon the sample preparation and the rate of heating (see Figure 1). Differential scanning calorimetry revealed that the solid underwent two exothermic reactions at *ca.* 160 and  $300^\circ\text{C}$ . The former reaction gives a much larger heat effect than does the latter (Figure 1). Mass spectroscopy of the initial solid showed the highest molecular ion peak at 172, which corresponds to  $\text{CSe}_2$  (for  $^{80}\text{Se}$ ). Both solids were found

to be amorphous to X-ray diffraction, similar to poly(carbon disulphide). The initial black solid was found to be electrically insulating (*ca.*  $10^{12}\ \Omega\text{ cm}$ ) but the second solid has an appreciable electrical conductivity (*ca.*  $10^{-3}\ \Omega^{-1}\text{ cm}^{-1}$ ). The i.r. spectrum of this second black solid was opaque down to at least  $600\text{ cm}^{-1}$ . This 'free carrier' absorption is consistent with the high conductivity.

It is well known that liquid phase reactions characterized by multiple bond formation are generally facilitated by application of hydrostatic pressure.<sup>4</sup> Thus the above observed

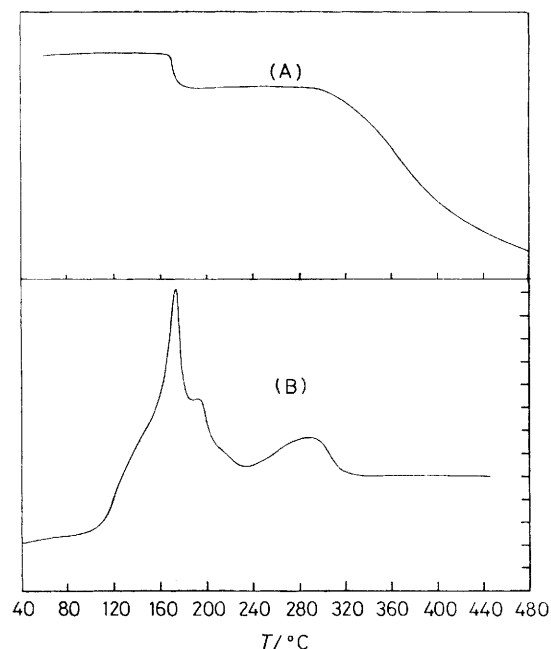
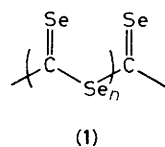
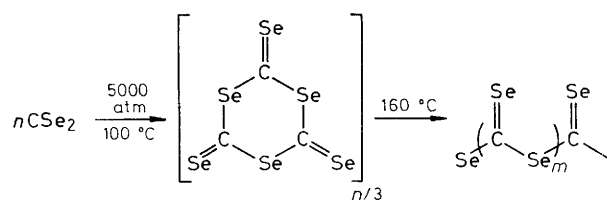


Figure 1. (A) Thermogravimetric analysis and (B) differential scanning calorimetric analysis of (1) under a nitrogen atmosphere.



results suggest that  $\text{CSe}_2$  reacted under high pressure to form an oligomer; probably a cyclic compound which then polymerized upon heating to  $160^\circ\text{C}$  to yield a linear polymer. The decrease in weight at *ca.*  $160^\circ\text{C}$  may be due to the elimination of unreacted trapped  $\text{CSe}_2$  or some decomposition of the solid during the polymerization. This reaction path is analogous to the formation of polyformaldehyde<sup>5</sup> and poly(nitrogen-sulphide)  $(\text{SN})_n$ <sup>6</sup> via their cyclic compounds.

Carbon diselenide was mixed with a large excess of carbon disulphide (molar ratio 1 : 10, respectively). When the solution was pressurized to 6000 atm and heated at  $100^\circ\text{C}$  for 10 h, only selenium-containing solid was obtained, which was

identified as the same product as that from the reaction of  $\text{CSe}_2$  in methylene chloride.

Carbon selenosulphide ( $\text{CSSe}$ ) was dissolved in methylene chloride or dioxan and then the solution was pressurized to 6000 atm and heated at  $120^\circ\text{C}$ . However, no detectable product was obtained; unchanged  $\text{CSSe}$  was recovered.

We are grateful to the Koppers Company, Inc., for support of this work with a generous grant.

Received, 22nd December 1981; Com. 1458

## References

- 1 D. Barnard and D. T. Woodbridge, *J. Chem. Soc.*, 1947, 1080.
- 2 A. J. Brown and E. Whalley, *Inorg. Chem.*, 1968, **7**, 1254.
- 3 T. Wentink, *J. Chem. Phys.*, 1958, **29**, 188.
- 4 K. E. Weale, 'Chemical Reactions at High Pressure,' E. and F. N. Spon, Ltd., London, 1967.
- 5 R. W. Lenz, 'Organic Chemistry of Synthetic High Polymers,' Interscience Publishers, New York, 1967, p. 550.
- 6 M. Goehring, *Quart. Rev.*, 1956, **10**, 437.