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HIGHLY CONDUCTIVE POLY(CARBON DISELENIDE)

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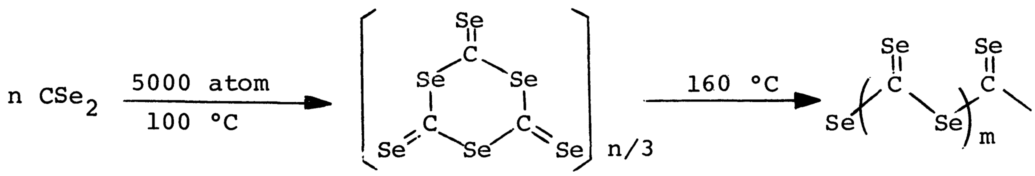
Crystalline poly(carbon diselenide) has been revealed to be a highly conductive material. The room-temperature resistivity is 0.06 Ω cm. The thermoelectric power is as small as those of normal metals. The X-ray photograph showed a sharp powder diffraction pattern.

Recent discoveries of organic superconductors[1,2] have caused an increasing interest in the field of synthetic metals. The organic superconductors ever known are composed of the planar donor molecules with chalcogen atoms (S or Se) in a π-conjugated system. Carbon diselenide CSe_2 is the simplest π-conjugated molecule with Se atoms.

Recently, Okamoto and Wojciechowski have reported the synthesis of a conductive polymer of carbon diselenide;[3] they proposed the following two step reactions.



The second step appears to be analogous to the solid state polymerization of S_2N_2 which affords a well-known inorganic polymer superconductor, $(SN)_x$.[4]

We have prepared highly conductive crystals of poly(carbon diselenide) as a black solid from purified CSe_2 by the procedure similar to that described by Okamoto and Wojciechowski who used a mixed solution of CSe_2 and methylene chloride (or dioxane).

The room-temperature dc resistivity of the compaction sample (0.06 Ω cm) is 10^4-10^5 times smaller than the reported value (10^3 Ω cm).[3] The resistivity increases gradually with decreasing the temperature. However, the value at 1.7 K is only 2-3 times larger than the room-temperature value (Fig. 1). The small and negative thermoelectric power (S) indicates the existence of conduction electrons. From the linear temperature dependence of S (T>50 K) (Fig. 2), the Fermi energy of the conduction electrons was estimated to be about 0.6 eV (60 kJ mol^{-1}), based on the simple free electron model.

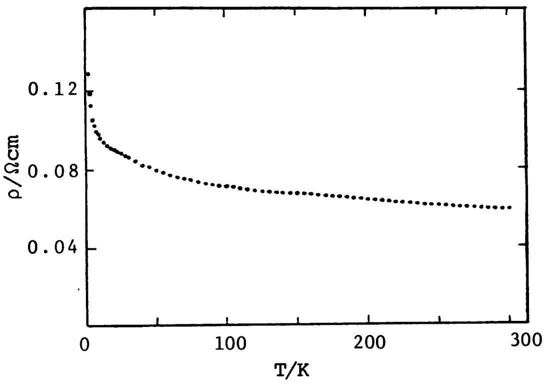


Fig. 1. Electrical resistivity of poly(carbon diselenide).

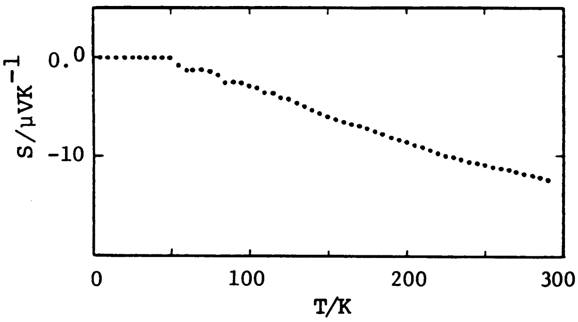


Fig. 2. Thermoelectric power (S/μV K^{-1}) of poly(carbon diselenide).

The solid of highly conductive poly(carbon diselenide) gave a sharp powder X-ray diffraction pattern (Fig. 3), while Okamoto and Wojciechowski have reported that their poly(carbon diselenide) is amorphous. These facts suggest that the solid poly(carbon diselenide) is highly conductive in an ordered crystalline state and it becomes less conductive when crystal imperfection increases. As reported by Okamoto and Wojciechowski, the black product of the first step reaction is insulating. So that, the polymerization (second step reaction) is essential for the appearance of the electrical conduction, which will produce a large sample dependence.

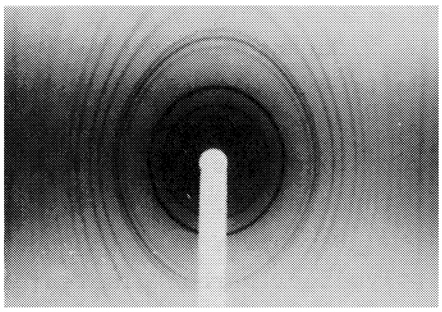


Fig. 3. X-Ray diffraction pattern of poly(carbon diselenide).

In summary, poly(carbon diselenide) was found to be a new highly conductive material. We can expect further increase in the electrical conductivity if the crystal growth process is improved.

References

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