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Synthesis and Electrical Conductive Property of New Tellurium Polymers Containing Thiocarbonyl Group

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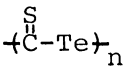
The new two thiocarbonyl telluride polymers, poly(thiocarbonyltelluride) and poly(thiocarbonylditelluride), were synthesized. The native polymers showed low electrical conductivities of 5.7 x 10^{-7} and 7.7 x 10^{-6} S cm^{-1} at room temperature, respectively. The doping of the polymers by I_2 or Br_2 brought an increase of 20 - 1000 times in the conductivities. Also, $HgCl_2$ somewhat exhibited a doping effect.

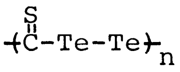
There is currently much scientific and technological interest in conductive polymers, of which polyacetylene is the first to be discovered.[1)] The native polyacetylene has the low-level electrical conductivity of a semiconductor. Reducing it with alkali metal puts electrons into the material's conduction band, significantly increasing its electrical conductivity.[2)] Also, oxidizing it with halogen or Lewis acid removes electrons from the valence band, causing positive vacancies that can conduct electrical current.[2)] The electrical conductivities of doped trans- and cis-polyacetylenes are seven orders of magnitude higher than those of the native polymers. The other polymers than polyacetylene, e.g., poly(p-phenylene), poly(p-phenylenevinylene), polypyrrole, and polythiophene etc., also showed high electrical conductivities by doping them. For these polymers the charge carriers created by doping essentially move on the π electron conjugated carbon chain. Of course, such a chain is not necessary to carbon systems. We have rather interest in polymer chain with long series of alternating carbon and tellurium atoms from aim at developing new electrical conductive polymers, which have combined properties of polyacetylene-like organic conductor and tellurium metal becoming a superconductor under the conditions of very low temperature and high pressure.[3)] In this paper we report the synthesis and electrical conductive property of new two tellurium polymers containing thiocarbonyl group, poly(thiocarbonyltelluride) (1) and poly(thiocarbonylditelluride) (2).

The thiocarbonyl telluride polymers were synthesized as follows. Di-



$\left(\overset{\overset{S}{\|}}{C}-Te\right)_n$

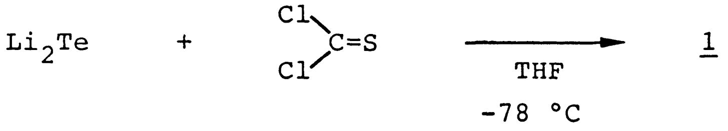
1

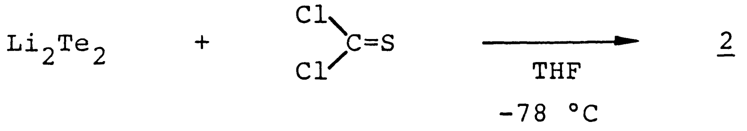


$\left(\overset{\overset{S}{\|}}{C}-Te-Te\right)_n$

2

lithium telluride (Li_2Te)[4] was treated with 2 equiv. of thiophosgene[5] in dry THF at -78 °C and the mixture was stirred for 12 h. The resultant precipitate was filtered and washed with THF, ethanol, and lastly carbon disulfide to afford a black powder (mp > 300 °C) in 20% yield. The elemental analysis (Found C: 6.49%; Calcd C: 6.99%) identified the powder with 1. Thiophosgene also was reacted with dilithium ditelluride (Li_2Te_2)[6] under the similar conditions, and the black powder of 2 (mp> 300 °C) was obtained in 19% yield: Found C: 4.41%; Calcd C: 4.00%. When these reactions were carried out at room temperature, the grey powder composed of almost Tellurium metal only was produced. Both 1 and 2 are stable in air, and insoluble in almost organic solvents. The polymerization number, n, could not be accurately determined, but was estimated less than 100 from the elemental analytical value of chlorine atom.[7]





The electrical conductivities of 1 and 2 at room temperature were measured in the compressed pellet states.[8] The value (σ_0) were 5.7×10^{-7} and 7.7×10^{-6} Scm^{-1}, respectively. The similar tendency to the larger σ_0 value of 2 than 1 also was observed in comparison between $(CH_2Te)_n$[9,10] and $(CH_2Te_2)_n$,[9] and between $(CH_2\text{-}C_6H_4\text{-}CH_2Te)_n$[11] and $(CH_2\text{-}C_6H_4\text{-}CH_2Te_2)_n$.[11] Now, the doping effect on the electrical conductivities was investigated. When the compressed pellets of 1 and 2 were exposed to I_2 or Br_2 vapor, their electrical conductivities gradually increased and reached maximum values (σ_{max}). The results are summarized in Table 1. For 1 there was a comparatively large increase of 20 - 1000 times. In contrast with this, for 2 the doping resulted in only an increase of 4 - 5 times. It was unexpected that the doping effect of 1 and 2 was less effective than those of nonconjugated tellurium polymers of $(CH_2Te)_n$, $(CH_2Te_2)_n$, $(CH_2\text{-}C_6H_4\text{-}CH_2Te)_n$,

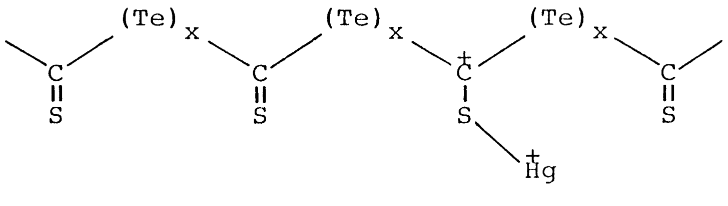
Table 1. The electrical conductivities of 1 and 2 before and after doping with I_2 or Br_2 vapor

Te-(C=S) polymer	σ_0 a) / S cm^{-1}	Dopant	σ_{max} b) / S cm^{-1}
1	5.7×10^{-7}	I_2	1.2×10^{-5}
		Br_2	5.7×10^{-4}
2	7.7×10^{-6}	I_2	3.0×10^{-5}
		Br_2	4.0×10^{-5}

a) Electrical conductivity before doping. b) Maximum electrical conductivity after doping.

and $(CH_2-C_6H_4-CH_2Te_2)_n$. Presumably, for doped 1 and 2 either the cation or the cation radical generated is not so effectively delocalized on the polymer chain because of poor conjugation through telluride or ditelluride groups.

Furthermore, by soaking 1 and 2 in a benzene solution containing 0.5 equiv. of $HgCl_2$ for a while, their electrical conductivities also increased albeit in a small effect. Thus, there was an increase of 10 times for 1 ($\sigma_0 = 5.8 \times 10^{-6}$ S cm^{-1}) and of ca. 4 times for 2 (2.8×10^{-5} S cm^{-1}), respectively. In particular, for 2 the doping effect by $HgCl_2$ almost was comparable with that by I_2 or Br_2. The Hg^{2+} ion is a soft acid and has strong affinity to soft bases of sulfur and tellurium atoms. In the present case it is most likely that Hg^{2+} is coordinated to the sulfur atom of thiocarbonyl group so as to create the cation carrier, which is responsible for the increasing electrical conductivity. The other metal ions than Hg^{2+}, e.g., Cu^{2+} and Cd^{2+}, exhibited very small doping effect.



x=1, 2

In summary, the conjugated polymers composed of thiocarbonyl-telluride or thiocarbonyl-ditelluride units were easily synthesized by the reaction of thiophosgene with Li_2Te or Li_2Te_2. This method might also be applied to the synthesis of sulfur and selenium analogues of 1 and 2 by using dilithium salts of sulfide, disulfide, selenide or diselenide in place of Li_2Te or Li_2Te_2. We are now under investigation of the synthesis of these polymers and of the doping effect on their electrical conductivities for comparison with the case of 1 and 2.

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5) Thiophosgene in various amounts was reacted with Li_2Te at -78 °C. In use of an equimolar amount 1 also was obtained, but the yield was very low. On the other hand, the use in 5 equiv. gave no precipitate because of only formation of various kinds of solvent-soluble lithium thiocarbonyl tellurides.
6) J. A. Gladysz, J. L. Hornby, and J. E. Grabe, J. Org. Chem., 43, 1204 (1978).
7) The polymers should bear chlorine atoms in both terminals, if no hydrolysis occurs. However, the elemental analyses and IR spectra showed the presence of hydroxy group due to partial hydrolysis.
8) The powder was compressed into a disk pellet, and its electrical conductivity was measured by two-probe method.
9) T. Nogami, T. Hasegawa, K. Inoue, and H. Mikawa, Polym. Commun., 25, 329 (1984).
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