New Conductive Aliphatic Tellurium Polymers: Poly(methylene Ditelluride) and Related Polymers

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Poly(methylene ditelluride), (**2**), and the related polymers (**1**), (**3**), (**4**), and (**5**), were found to give conductive materials (10^{-2}—10^{-7} S cm^{-1}) upon doping with bromine or iodine.

Studies on highly conducting polymers have progressed greatly since the discovery of the polymeric superconductor $(SN)_x$[1] and the metallic conducting organic polymer, $(CH)_x$.[2] The high conductivities of the polymers were realized by doping them with electron donor or acceptor molecules, with the exception of $(SN)_x$. However, most of the polymers doped were unstable in air. The replacement of nitrogen with CH and of sulphur with Se or Te in $(SN)_x$ will give useful polymers, *e.g.*, $(CHSe)_x$ and $(CHTe)_x$, and they are expected to be highly conducting without doping. It is not known whether or not such polymers are stable at room temperature. We have synthesized the related polymers, $(CH_2Te)_x$ (**1**), $(CH_2Te_2)_x$ (**2**), $(CH_2Se)_x$ (**3**), $(p\text{-}CH_2C_6H_4CH_2Te)_x$ (**4**), and $(p\text{-}CH_2C_6H_4CH_2Te_2)_x$ (**5**).[3] We have found that they belong to a new class of electrically conducting material upon doping with acceptor molecules.

Table 1. Aliphatic tellurium polymers; the degree of polymerization (x), dopant, the electrical conductivity before doping (σ_0), the maximum electrical conductivity upon doping (σ_{max}), the time required to attain to the maximum conductivity (t_{max}), and the doping ratio.

Polymer	x	Dopant	σ_0/S cm^{-1}	σ_{max}/S cm^{-1}	t_{max}/h	Doping ratio/%
(1)	>2000	Br_2	2×10^{-10}	3×10^{-5}	0.8	4.4
		I_2		1×10^{-9}	16	1.1
(2)	120	Br_2	4×10^{-5}	4×10^{-2}	1	15.8
(3)	1000[a]	I_2	2×10^{-9}	2×10^{-3}	5	12.0
	200[b]	Br_2		4×10^{-4}	[c]	[d]
		$SbCl_5$		6×10^{-4}	[c]	[d]
(4)	90	Br_2	3×10^{-12}	2×10^{-3}	2.8	9.7
		I_2		1×10^{-7}	2	13.4
(5)	20	Br_2	3×10^{-12}	2×10^{-4}	1.7	15.8
		I_2		1×10^{-7}	22	8.0

[a] Polymer was obtained by reacting Li_2Se with CH_2I_2. [b] Polymer was obtained by reacting Li_2Se with CH_2Br_2. [c] Very fast. [d] Doping ratio could not be obtained because of the gasification of the polymer upon doping.

$(CH_2Te)_x$
(1)

$(CH_2Te_2)_x$
(2)

$(CH_2Se)_x$
(3)

$(p\text{-}CH_2C_6H_4CH_2Te)_x$
(4)

$(p\text{-}CH_2C_6H_4CH_2Te_2)_x$
(5)

The polymers **(2)**, **(3)**, **(4)**, and **(5)** were obtained by the reaction of superhydride ($LiBEt_3H$) with elemental Te in tetrahydrofuran [Se in the case of **(3)**], followed by the reaction of the resultant Li_2Te, Li_2Te_2, or Li_2Se with the corresponding aliphatic dibromides or di-iodides in an inert atmosphere at room temperature.[3] Since this procedure gave **(1)** only in poor yield (3%), **(1)** was synthesized as follows. The polymer **(2)** was treated with $NaBH_4$ in methanol for six hours under a nitrogen atmosphere at room temperature, and the intermediate **(6)** was then converted into **(1)** in relatively high yield (70%) on addition of CH_2Br_2 or CH_2I_2, equation (1).

$$(CH_2Te_2)_x + 2x\,NaBH_4 \longrightarrow \underset{\textbf{(6)}}{x\,Na^{+}\,{}^{-}TeCH_2Te^{-}\,Na^{+}} \xrightarrow[CH_2I_2]{CH_2Br_2\ \text{or}} \textbf{(1)} \qquad (1)$$

All of the aliphatic tellurium polymers were purified by stirring with aqueous KCN for several hours in order to dissolve the elemental Te present as an impurity. For the purification of **(3)**, Na_2S was used instead of KCN. *X*-Ray diffraction of the powdered polymers gave several sharp diffraction patterns except for **(4)**, which suggests microcrystalline structures. Differential scanning calorimetry and thermogravimetric analysis of the polymers revealed that all of them decompose above 200 °C.

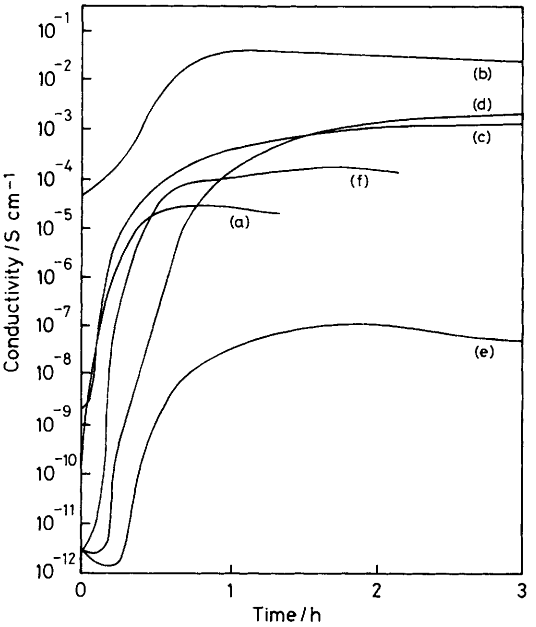

Figure 1. Time dependence of the electrical conductivity of aliphatic tellurium polymers upon doping with bromine or iodine. (a) **(1)** + Br_2, (b) **(2)** + Br_2, (c) **(3)** + I_2, (d) **(4)** + Br_2, (e) **(4)** + I_2, (f) **(5)** + Br_2.

Table 1 gives the degree of polymerization (x), the dopants, the electrical conductivities before doping (σ_0), the highest electrical conductivity at room temperature upon doping with bromine or iodine (σ_{max}), the time required to attain the highest conductivity (t_{max}), and the doping ratio relative to monomer units at the highest conductivity. Since these polymers were insoluble in the usual organic solvents, the degree of polymerization could not be obtained by usual methods. Since the terminal group of the polymers is assumed to be bromide,† the degree of polymerization can be estimated from the intensities of the *X*-ray fluorescence due to Te and Br as follows. The curves of the intensity ratio of *X*-ray fluorescence due to Te and Br were plotted against the atomic ratio of Te and Br for several mixtures of elemental Te with *p*-dibromobenzene. The degree of polymerization was then estimated from the curve. The values ranged from 20 to 2000. The doping ratios were estimated from the increase in weight upon doping.

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† The terminal groups are assumed to be either Br or TeH. However, the TeH group is known to be unstable toward air oxidation to give ditelluride (see ref. 4).

The changes in electrical conductivity of the polymers upon doping with bromine or iodine were measured by the procedures reported,[5] and are shown in Figure 1. Bromine doping of (**1**), (**2**), (**4**), and (**5**), increased their electrical conductivities by four to nine orders of magnitude to 10^{-2}—10^{-6} S cm^{-1} within three hours. The conductivity of (**3**) also increased by five orders of magnitude upon doping with iodine. The highest conductivity (4×10^{-2} S cm^{-1}) was obtained for (**2**) upon bromine doping, $(CH_2Te_2Br_{0.158})_x$. A parallel relationship was observed between the doping ratio and the electrical conductivity. The electrical conductivity of all of the polymers decreased slowly after reaching the maximum. Since organic tellurium compounds are known to be reactive towards halogen, the decrease in conductivity will be caused by irreversible chemical reactions. The conductivity of (**3**) reached *ca.* 10^{-4} S cm^{-1} by doping with Br_2 or $SbCl_5$, and then gasified by a violent reaction. The electrical conductivity of (**2**) before doping (4.3×10^{-5} S cm^{-1}) was one order of magnitude lower than that reported by Wudl (5×10^{-4} S cm^{-1}).[6] Although the reason for this difference is not clear, it may result from the difference in the molecular weight and/or morphology, because a different synthetic method for (**2**) was used.

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