Letters to the Editor

ELECTRICAL CONDUCTIVITY AND MORPHOLOGY OF POLYACETYLENE PREPARED BY TITANIUM(III) AND TITANIUM(IV) COMPLEXES

ЭЛЕКТРОПРОВОДНОСТЬ И МОРФОЛОГИЯ ПОЛИАЦЕТИЛЕНА, ПРИГОТОВЛЕННОГО КОМПЛЕКСАМИ ТИТАНА(III) И ТИТАНА(IV)

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Polyacetylene, $(CH)_x$, has been extensively studied since it was shown [1] that with suitable dopants this polymer can form highly conducting complexes with unusual physical properties. Studies concentrated mostly on free standing polyacetylene films prepared by techniques of Ito et al. [2] using the catalyst $Ti(OC_4H_9)_4$—$Al(C_2H_5)_3$. Polyacetylene synthetized by other catalytic systems has been investigated only rarely [3—5].

The present contribution compares electron scanning micrographs and temperature dependences of the DC electrical conductivity after doping with iodine of polyacetylene prepared by two different catalytic systems: tetrahydrofuran solution of $TiCl_3$ and $Mg(C_5H_5)_2$ (resulting in a black powder material) and hexane solution of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$ (the above-mentioned free standing films).

Powder polyacetylene was prepared by catalytic polymerization of acetylene by a catalytic system containing $TiCl_3L_3$ (L = molecular ligand) and $Mg(C_5H_5)_2$ in tetrahydrofuran solution using techniques of Zikmund et al. [6]. Polyacetylene films were synthetized from acetylene on the surface of a catalytic hexane solution of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$ at room temperature by techniques of Ito et al. [2] and thermally isomerized in vacuo at 175 °C for 25 minutes to all *trans*-polyacetylene.

Both powder and film samples were doped by exposure to iodine vapour at a pressure of 10 Pa. The doped samples were pumped for about one hour, then the dopant concentration y, defined as the number of iodine atoms per one CH unit of the polymer, was determined from weight uptake of the sample. Undoped, as well as doped powder polyacetylene was compressed into free standing pellets,

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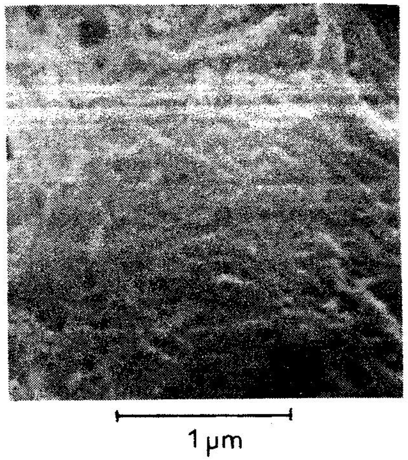
Fig. 1. Electron scanning micrograph of powder polyacetylene prepared by a catalytic solution of $TiCl_3$ and $Mg(C_5H_5)_2$.



except for very heavily doped samples with dopant concentrations of $y > 0.10$, which we were not able to compress into pellets with satisfactory mechanical properties.

Four platinum wires were attached to the film or to the perimeter of the pellet by means of the graphite paste Dag 580 that was found to form ohmic contact with our samples. The DC conductivity was measured from 77 K to 295 K using the standard four—probe method for the films and van der Pauw's [7] method for the pellets. For the most resistant samples (films with $y \leq 0.08$ and the pellet with $y = 0$) a two-probe method was used.

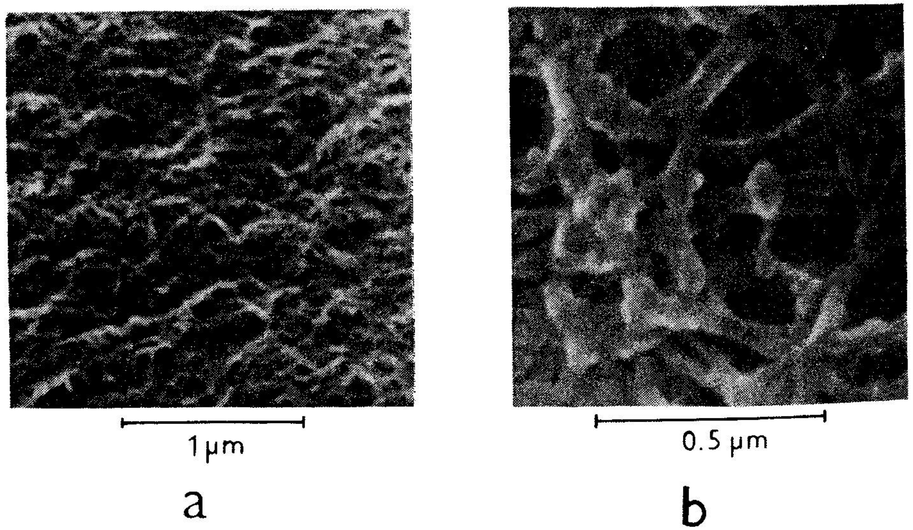


Fig. 2. Electron scanning micrographs at different magnifications of a polyacetylene film prepared by a catalytic solution of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$.

The electron scanning micrograph of the polyacetylene powder is shown in Fig. 1. Micrographs of a polyacetylene film are shown in Fig. 2. in two different magnifications. The two materials have a comparable fibrous morphology with fibers of a diameter of 30—60 nm. Differences can be seen on a larger scale, where the powder material (Fig. 1) is rather non-homogeneous in comparison with the large scale uniformity of the film (Fig. 2a).

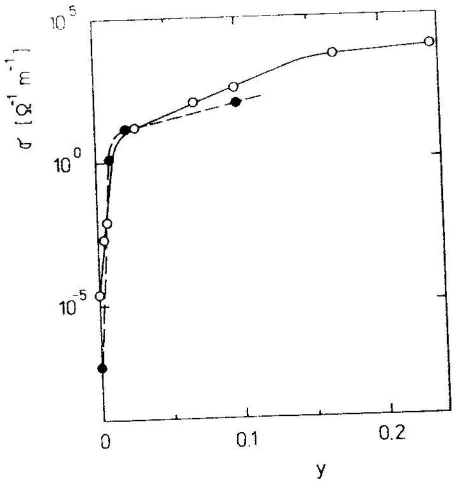


Fig. 3. Room temperature DC conductivity of iodine doped polyacetalene as a function of the dopant concentration y: —●— powder materials prepared by a catalytic solution of $TiCl_3$ and $Mg(C_5H_5)_2$, —○— films prepared by a catalytic solution of $Ti(OC_4H_9)_4$ and $Al(C_2H_5)_3$.

The room temperature DC conductivity of the two forms of polyacetylene as a function of the dopant concentration y is shown in Fig. 3. For boths forms of polyacetylene we have observed a rapid increase of conductivity in the concentration region from $y = 0$ to a critical concentration $y_c \approx 0.01$ and a tendency to saturation for heavily doped samples with concentrations of $y > y_c$, in agreement with earlier measurements [8] on iodine doped polyacetylene films. At a given dopant concentration, values of conductivity of the two materials are approximately the same. If one wants to compare conductivities of these two forms of polyacetylene, it is necessary, however, to take into account that 1) the powder material was a nonisomerized mixture of *cis*- and *trans*-polyacetylene, while the films were all *trans*-polyacetylene; the presence of the *cis*-component can lead to a smaller conductivity (observed in our case) of the undoped sample [9] and a slightly higher conductivity of the doped samples [10], 2) the volume filling ratio of non-compressed polyacetylene is less than unity (see Fig. 1 and Fig. 2), so that the conductivity measured on compressed pellets with the volume filling ratio equal to unity has to be reduced correspondingly.

The temperature dependence of the DC conductivity of polyacetylene powder in the temperature range of 77 K—295 K for various dopant concentrations y is plotted in Fig. 4 as log σ versus $T^{-1/4}$. The same dependence for polyacetylene films is shown in Fig. 5. We have observed no difference in behaviour of the temperature dependences of the conductivity in the two investigated materials. The conductivity decreases with decreasing temperature for all dopant concentrations and plots of log σ versus $T^{-1/4}$ manifest an approximately straight-line behaviour, i.e. $\sigma = \sigma_0 \exp(-(T_0/T)^{1/4})$, in agreement with earlier studies [8, 11] of iodine doped polyacetylene films. Temperature dependence of this form is usually ascribed to the mechanism of a three-dimensional variable range hopping between localized states [12].

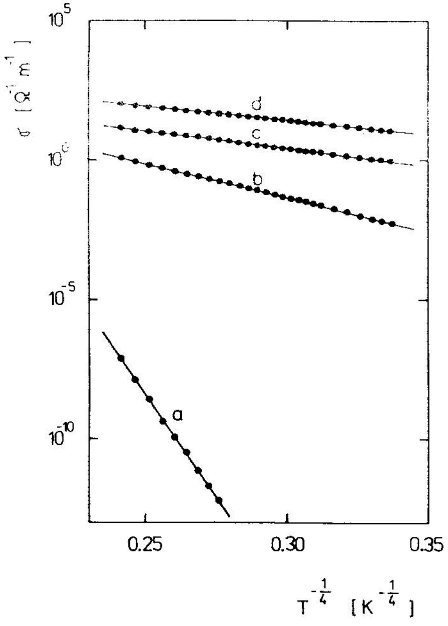


Fig. 4. log σ versus $T^{-1/4}$ of iodine doped polyacetylene powder with various iodine concentrations y: (a) $y=0$, (b) 0.010, (c) 0.022, (d) 0.10.

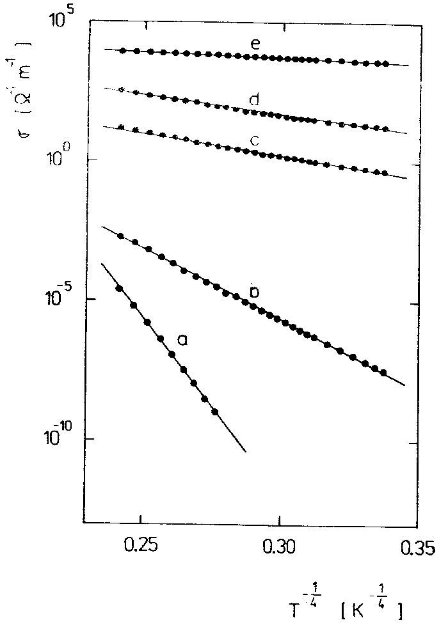


Fig. 5. log σ versus $T^{-1/4}$ of iodine doped polyacetylene films with various iodine concentrations y: (a) $y=0$, (b) 0.004, (c) 0.028, (d) 0.10, (e) 0.24.

Concluding, we have shown that polyacetylene powder prepared by a catalytic solution of $TiCl_3$ and $Mg(C_5H_5)_2$ and polyacetylene films prepared by a catalytic solution of $Ti(OC_4H_9)_6$ and $Al(C_2H_5)_3$ have a comparable fibrous morphology and that values of the DC electrical conductivity after doping with iodine, as well as its temperature dependences of the type $\sigma = \sigma_0 \exp(-T_0/T)^{1/4}$ in the two materials are similar.

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