The Relationship of the Conductivity of Polyacetylene to the Average Length of Double-bond Conjugation

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Using partially hydrogenated polyacetylene films doped with I_2, the electrical conductivity was found to depend strongly upon the length of double-bond conjugation.

The semiconducting polyacetylene film exhibits a marked increase in electrical conductivity when chemically doped with various donors and acceptors,[1] and hence a number of investigations have been carried out on the electrical conductivity of doped polyacetylene films.[2] Few studies have been concerned, however, with the relationship of the conductivity to the length of double-bond conjugation.

We have recently found that alkali metal-doped polyacetylene films are partially hydrogenated in a random way by their exposure to methanol.[3] We have now prepared polyene films with various lengths of double-bond conjugation using this method and examined their conductivity.

Sodium-doped polyacetylene films were prepared by treating *trans*-polyacetylene films[1,4] with a tetrahydrofuran (THF) solution of sodium naphthalide (*ca.* 0.5 M) followed by repeated washing with THF until the resulting THF solution became colourless and *in vacuo* drying at room temperature. The Na-doped polyacetylene films thus obtained were treated with liquid methanol for times ranging from 3 min to 72 h. The Na contents of the doped films were determined by titration of the solution from the THF washing with aqueous 4×10^{-4} M HCl. It has been established that the uptake of hydrogen is equal to the amount of Na in the original films and that the hydrogenation takes place in a random way.[3]

The recovered polyene films were dried *in vacuo*, and then exposed to I_2 vapour (*ca.* 0.2 mmHg) for times ranging from 5 min to 2 h. The uptake of I_2 was determined by weighing the films. The *X*-ray diffraction spectra of the polyene displayed a sharp diffraction peak at $2\theta = 23°$ indicative of very high crystallinity.

The average length of double-bond conjugation was estimated from the amount of hydrogen uptake assuming a completely random hydrogenation. Figure 1 shows the relationship of the conductivity to the uptake of I_2 (y) for I_2-doped polyenes with various lengths of double-bond conjugation {l where l is the number of conjugated units in $-[CH{=}CH]_l-$}. It should be noted that the relation, $\ln \sigma / \ln y = 3$, is established for each polyene.[5] Figure 2 shows the relationship of the conductivity of the I_2-doped polyenes ($\sigma_{0.1}$ at $y = 0.1$) to the average length of double-bond conjugation (l). It is of great interest that the relation, $\ln \sigma / \ln l = 3.5$, is established between them.

The result clearly indicates that the electrical conductivity

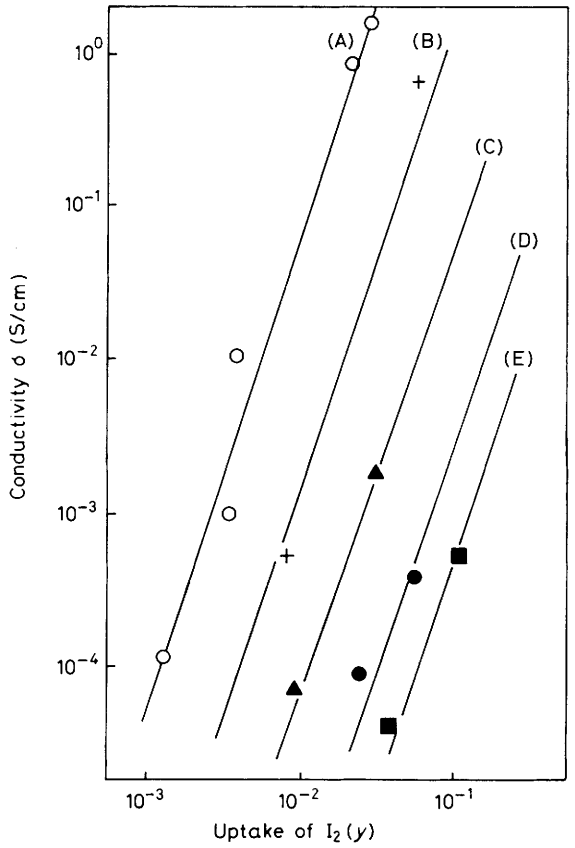

Figure 1. Relationship of the conductivity (σ) to the uptake of I_2 (y). D.c. conductivities were measured on films using standard two- or four-point probe techniques. (A) Original polyacetylene ($l = 200$); polyenes (B) 0.9% hydrogenation ($l = 100$); (C) 4% ($l = 25$); (D) 8% ($l = 13$); (E) 10% ($l = 10$).

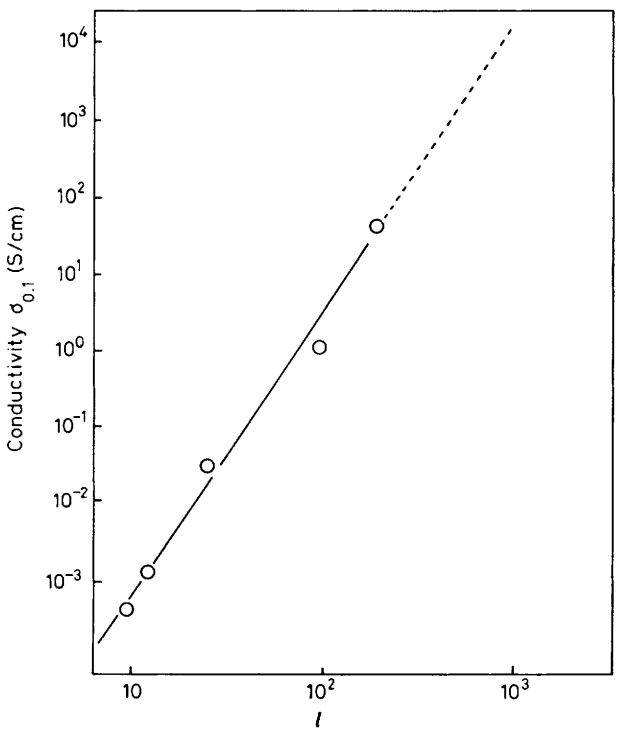

Figure 2. Linear relation of the conductivity at $y = 0.1$ ($\sigma_{0.1}$) to the average length of double-bond conjugation (l).

of polyacetylene is strongly dependent upon the length of double-bond conjugation.

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