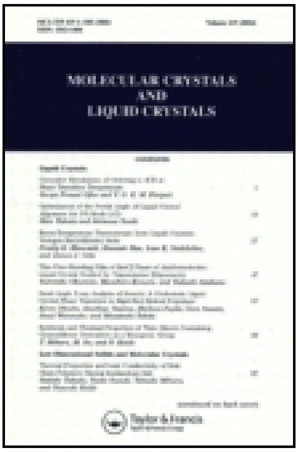

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Anisotropy of Charge Transport Properties in Highly Conductive Oriented Polyacetylene

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ANISOTROPY OF CHARGE TRANSPORT PROPERTIES IN HIGHLY CONDUCTIVE ORIENTED POLYACETYLENE

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Abstract Electrical conductivity and thermopower of two types of highly conductive polyacetylene are presented. The anisotropy of the charge transport properties is discussed in consideration of an inhomogeneous structure of polyacetylene.

INTRODUCTION

Charge transport in doped polyacetylene results from the presence of Π-conjugated chains. However, the flow of charges over a real macroscopic sample is determined by various conjugation breaking barriers. By mechanical stretching of a polyacetylene film it is possible to introduce an ordering into the molecular-chain structure and fibrylar superstructure of the material. This alignment should imply different properties of conduction when the current is flowing in parallel and in perpendicular to the stretching direction.

In this paper we present the analysis of electrical conductivity and thermoelectric power for highly conductive, stretch - -oriented doped polyacetylene. Our main interst is focused on the anisotropy of charge transport.

EXPERIMENTAL

Our experiments have been performed on two types of new polyacetylene. The first was decaline polyacetylene (DPA) synthesized following Tsukamoto[1] and the second - the cumene polacetylene (CPA) prepared following the procedure originally published by Akagi[2]. The details of synthesis and the preparation are published elsewhere [3,4]. The samples were stretched after drying and in the case of CPA also in the wet form with using a plasticizing mixture (cumene toluene 1:4). The maximum stretching ratio for DPA was only 2, whereas for CPA it reached 6. The polyacetylene samples were doped with iodine up to a saturation level (7% molar ratio).

RESULTS AND DISCUSSION

In fig.1a the relative conductivity for DPA is presented. The experimental curves $\sigma(T)/\sigma(RT)$ obtained for measurements performed in the parallel and perpendicular directions of oriented sample (in respect to the stretching direction) and also for the isotropic one are almost identical. The slight difference of the curves' shape is visible only above the flat maximum. In fig.2 the anisotropy of conductivity and also the ratio $\sigma\ /\sigma_{isotr}$ are plotted versus temperature. In the case of DPA the both ratios are almost constant over the whole T-range. Fig.1b shows conductivity data for CPA samples stretched 6 and 3 times. The anisotropy ratio is now much higher. Curves $\sigma(T)$ are more sloped in comparison to plots of DPA and they have no maximum. Like in the case of DPA the anisotropy is almost

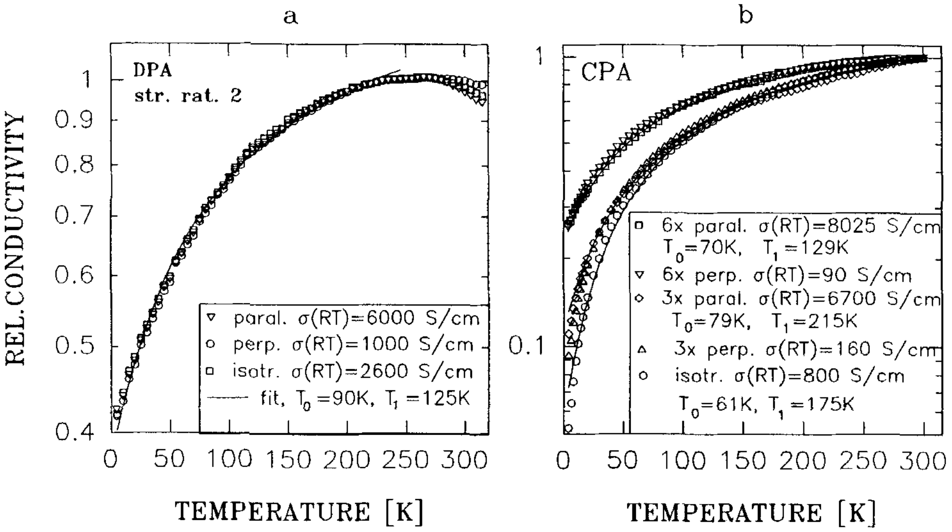

FIGURE 1 Normalized conductivity of DPA (a) and CPA (b). Solid line - fit to the Sheng's formula

constant within the whole temperature range (fig.2a). The behaviour of isotropic sample differs, however, from oriented ones. The $\lg\sigma(T)$ plot for not-oriented sample does not lie in parallel to the two oriented ones. It is much curved and steep. This feature is manifested as a monotonic decrease of $\sigma_{\|}/\sigma_{isotr}$ (fig.2b).

A quantitative interpretation of experimental $\sigma(T)$ functions can be achieved by fitting the results to the Ping Sheng[6] formula:

$$\sigma = \sigma_0 \exp((-T_1/(T_0+T))$$

originally derived to explain the conductivity of a heterogeneous material, consisting of highly conductive regions separated by potential barriers. The parameters T_0 and T_1 depend on the effective width and area of these barriers and the fluctuation induced tunneling determines the charge motion. Thus the width and area of non-conductive regions define the shape of the function $\sigma(T)$. The room temperature conductivity and, consequently, the anisotropy of conductivity depends mainly on the preexponential factor σ_0, which can be ascribed to the number or density of potential barriers within a current path.

For polyacetylene as a material of fibrilar morphology usually both intrafibrilar and interfibrillar barriers are considered when

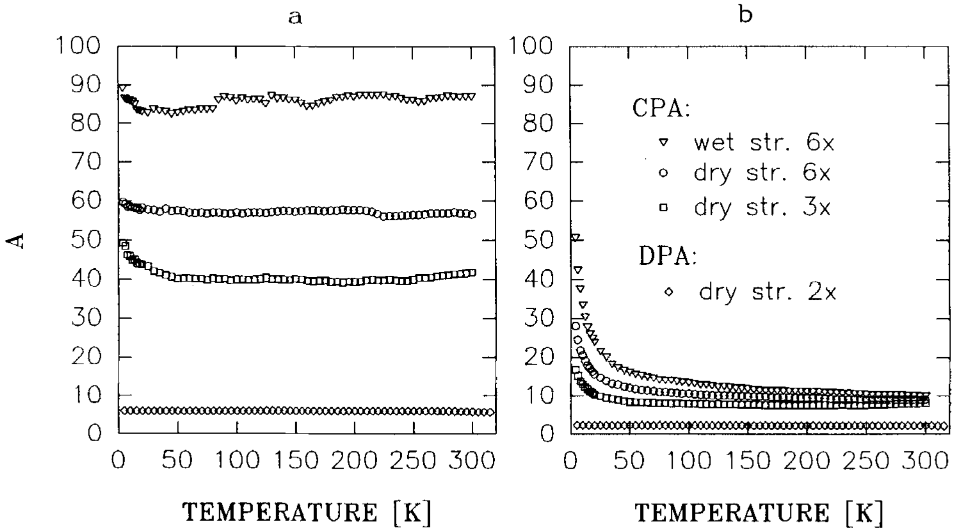

FIGURE 2 Anisotropy of conductivity (a) and the ratio $\sigma_{\|}/\sigma_{isotr}$ (b) for DPA and CPA stretched in dry and in wet form.

its transport properties are discussed. Because of geometrical reasons their contributions into charge transport occurring in two perpendicular directions should differ significantly. The constant value of the conductivity anisotropy indicates that only intrafibrillar barriers are active in the conduction of the electrical charge in both directions. The concept of insulating fiber surface stays in agreement with the results of our experiments on rolled polyacetylene[7]. Consequently, the transport limiting mechanism is quantitatively the same in oriented as in isotropic DPA (low stretchability) and in both directions of stretched CPA. In the case of CPA, however, although the fitting parameters T_0 and T_1 are identical for both directions of oriented sample, they differ significantly to analogical parameters of isotropic CPA. This means, according the Sheng's model, that mechanical stretching (at least above some ratio) results not only in change of inner geometry of polymer fibers but also changes the width and area of potential barriers. Since the width is proportional to T_1/T_0 ratio and the area - to T_1 we can state that due to mechanical ordering the barriers become narrower and less extended. Since the barriers are frequently identified as an undoped region[7] we can conclude that the stretching leads to the much homogeneous structure of polyacetylene and to decrease of some defected area which disturb the homogeneous doping.

In presented figures a small increase of the anisotropy can be noticed at low temperatures. Formally this feature can be explained as a consequence of slight disagreement of experimental curves with fitting formula. Physically this fact may be a result of a slight T-dependant contribution of a interchain hopping (having its own temperature dependence) which is much pronounced for current flowing perpendicularly to the direction of the oriented chains.

Another result of complexity of the charge transport in polyacetylene is different curvature of $\sigma_{\parallel}(T)$, $\sigma_{\perp}(T)$ and $\sigma_{isotr}(T)$ observed for DPA at temperatures above the maximum. The negative value of $d\sigma/dT$ is just what is expected from quasi 1-D metallic conduction within the conjugated chains, where the charge carriers are scattered by thermally excited $2k_F$ phonons. Because of the ordering of metallic strands the above effect is more evident in the case of parallel conduction.

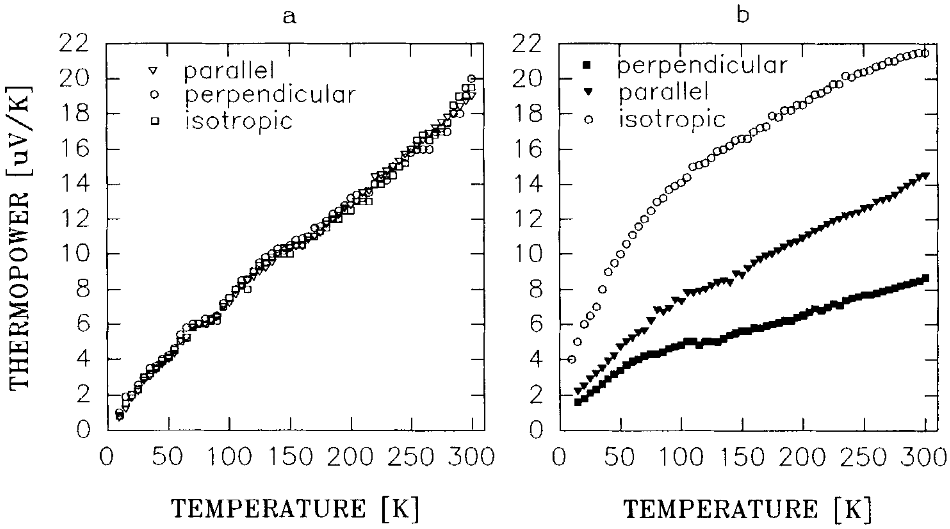

FIGURE 3 Thermopower of DPA (a) and CPA (b) measured in parallel and in perpendicular to the stretching direction for oriented samples and also for isotropic ones.

Fig.3a shows the temperature dependence of thermopower measured in two directions for oriented DPA and for unoriented samples. In fig.3b analogical experimental curves obtained for CPA are presented. In the first case the absolute values of the Seebeck coefficient as well as the shape of the S(T) function are identical for parallel, perpendicular and isotropic measurements. This feature confirms the earlier analysis of the anisotropy of conductivity. Since the thermopower is a "zero-current phenomenon" it does not depend on the inner geometry of fibers unless it does not influence the heat flow. Taking into consideration that in DPA the degree of ordering is rather low and barriers are not active in the heat conduction, the above condition seems to be fulfilled.

In the case of the more stretchable CPA ,however, the experimental curves $S_{\parallel}(T)$, $S_{\perp}(T)$ and $S_{isotr}(T)$ differ significantly. Moreover in the whole temperature range $S_{isotr}>S_{\parallel}>S_{\perp}$. Our experimental results can be explained if one considers the diverse contribution into the thermopower, originating from the metallic regions (S_M) and from barriers (S_B).In the case of the parallel measurements the majority of them are connected in series. Since the barriers are narrow the resulting thermopower is determined mainly by metallic phase[3]. In our schematic picture the thermopower measured in the perpendicular direction involves some microcircuits of parallel connected regions of low resistance and low thermopower with barriers areas characterized by high resistance and higher thermopower. Assuming that a heat flow is not disturbed on the fibers surface a preliminary rough calculation[3] based on the above model gives the ratio $S_{\parallel}/S_{\perp} > 1$.

CONCLUSIONS

The mechanical stretching of the polyacetylene foil leads to two effects. At the beginning it causes a geometrical ordering of entangled fibrils or drawing out the fibrils from the globules which areelements of pristine morphology. During this step most of the anisotropy is created. Assuming the constant density of the stretched material the parallel conductivity should increase in proportionality to the stretching ratio squared. The limit stretching ratio of this step lies between 2 and 3 depending on the type of synthesis. Further stretching results in only minor increase of conductivity but changes the shape of the temperature dependence of conductivity suggesting the modifications of the barrier structure.

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