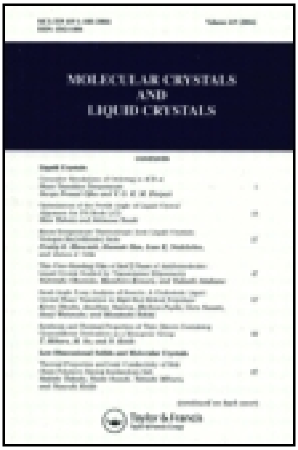

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N-Type Doping of Polyacetylene ESR Study Versus Temperature

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N-TYPE DOPING OF POLYACETYLENE: ESR STUDY VERSUS TEMPERATURE

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Abstract We have studied the evolution with temperature 300 K $\leq$ T $\leq$ 500 K of the ESR characteristics, on Lithium doped cis-polyacetylene films (using metal complexes of Benzophenone or Naphthalene in THF). Asymmetric ESR lines were observed at R T for samples doped at ~4% and ~16%. Annealing of the doped samples up to 500 K results in a significant irreversible increase of the peak to peak linewidth ΔH_{pp} at RT, while the asymmetry ratio A/B increases irreversibly only in the case of samples doped at ~4%. Nevertheless for temperatures above 400 K a narrow ESR line ($\Delta H_{pp} < 1$G) superposed on the asymmetric broader line was observed. In order to interpret these temperature behaviors, we suggest a model which takes into account the inhomogeneity of the dopant distribution and the solvent influence.

EXPERIMENTAL TECHNIQUES

The polyacetylene films, prepared using the Shirakawa technique[1], were 2x8x0,4 mm pieces of cis-rich $(CH)_x$. Doping was carried out by immersing the $(CH)_x$ films in a 0.02 M solution of Li-Benzophenone dianionic complex in THF or in a 0.3 M solution of Li-Naphthalene in THF, over a given time, as described previously[2]. After drying the sample was pumped for several hours by constant cryogenic pumping and sealed. The ESR spectra were obtained, using an ER 200 D Bruker spectrometer, working at 9.6 GHz.

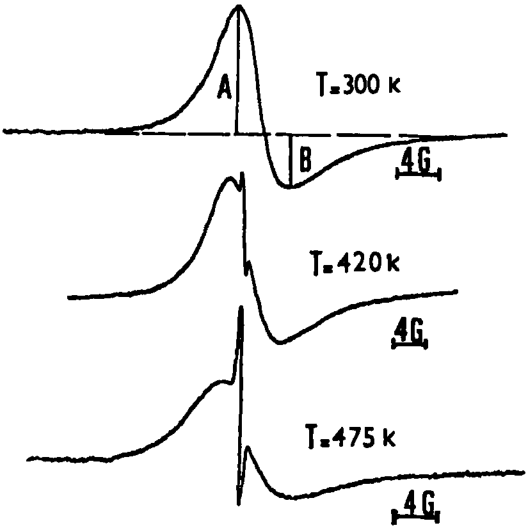

FIGURE 1 Evolution of the ESR signal of Li-doped cis-$(CH)_x$ during the annealing process.

RESULTS AND DISCUSSION

1- Cis-$(CH)_x$ Li-doped at ~4%.

As shown on the figure 1, the ESR spectrum of the doped cis-$(CH)_x$ films is asymmetric at RT, characterized by $\Delta H_{pp} \simeq 4,5$ G, and $A/B \simeq 2,5$ indicates that the system has reached the metallic state. A significant decrease of the linewidth from 4,5 to 0,9G was observed at RT, after cryogenic pumping of the doped samples for several hours, which is known to affect the degree of solvation of alkali dopants[3]. Then it seems that the solvation of the cations Li^+ significantly influences the linewidth, suggesting an important contribution to the linewidth of the spin-orbit interaction with the dopant.

Annealing of the doped films in the range 300 to 500 K results in a significant modification of the ESR characteristics.

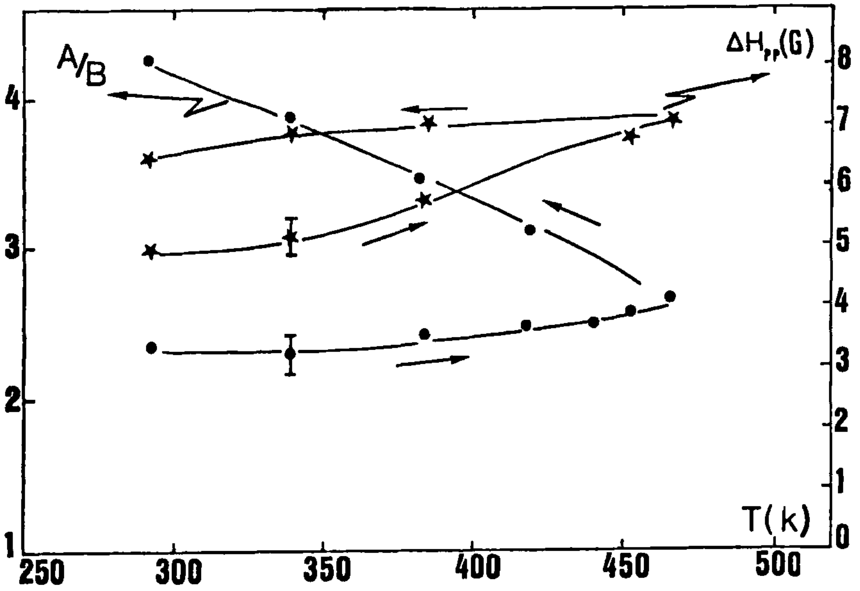

FIGURE 2 Variation of the ESR line asymmetry A/B and the linewidth ΔH_{pp} of Li-doped cis-$(CH)_x$ at ~4%, as a function of annealing temperature.

For T ≥ 400 K a narrow ESR line superposed on the asymmetric broader line appeared and persisted during the annealing process. The two lines are characterized by the same g value ($g \simeq 2.0026$), Fig. 1. In order to explain the appearance of the narrow line during annealing, we notice that the dopant distribution is usually inhomogeneous in the material [2,4] and that the cis-trans isomerization induced by the chemical doping is not fully achieved at ~4% doping level as evidenced by recent NMR results [5]. Consequently, the thermal treatment induces the isomerization of the remaining cis parts of the chains, yielding the appearance of the narrow line which can then be assigned to undoped trans sequences. Nevertheless, from the relative amplitude of the two superposed lines, we have estimated that the narrow line represents less than 1/100 of carbon atoms in the undoped trans situation.

The evolution with temperature of the ESR signal characteristics (A/B and ΔH_{pp}) is shown in Figure 2. We notice the irreversible increase after annealing of the asymmetry ratio A/B at RT from 2.3 to 4.2 which can be related to an increase of the conductivity [6,7] of the doped samples, due to the annealing effect. Irreversible increase after annealing of ΔH_{pp} at RT from ~5 G to ~6.5 G was also observed. It is reasonnable to assume that desolvation of the cations occurs during the thermal treatment, yielding an increase of the spin-orbit interaction with the dopant and then the ΔH_{pp} increase. The observation of the non reproducibility of A/B and ΔH_{pp} at RT after annealing can be assigned to a change in solvation and also could be possibly due to a structural rearrangement [8] occuring during the isomerization of the remaining cis sequences of the chains.

2- Cis-$(CH)_x$ Li-doped at ~16%.

As presented in Figure 3, the variation with temperature of ΔH_{pp} is similar to the preceding case. On the contrary, there is no significant variation with temperature of A/B which is reversible after annealing at RT, (A/B $\simeq$ 2.7) and also no appearance of a superposed narrow line, during annealing. The absence of a narrow line in this case can be interpreted as a consequence of a better homogeneity of the dopant distribution in the system and the complete chemically induced isomerization of the polymer. The absence of a significant variation with temperature of A/B can be related to a high conductivity of the material [6,7]. Thereby, no indication of the evolution of the conductivity can be deduced from the ESR line asymmetry, during annealing. The irreversibility of ΔH_{pp} after annealing, at RT can be attributed to the same mechanisms as mentioned in the preceding case.

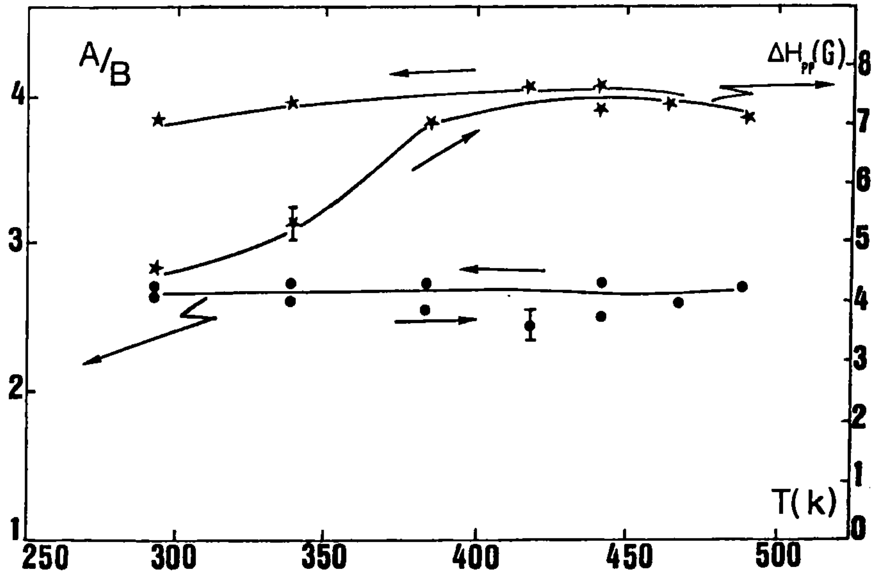

FIGURE 3 Variation of the ESR line asymmetry A/B and the linewidth ΔH_{pp} of Li-doped cis-$(CH)_x$ at $\sim$6%, as a function of annealing temperature.

According to the results described above, we note that:

- the conductivity of Li-doped cis-$(CH)_x$ is still high after annealing at high temperature, indicating that the system is very stable.
- the observed irreversibility of A/B and ΔH_{pp} after annealing at RT, can be attributed to a change in the cations solvation and possibly to a structural rearrangement during annealing.

One way to answer this last question is to study the evolution with temperature of the n-doped polyacetylene structure, using ^{1}H NMR spectroscopy for instance. Such studies are now under progress.

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