Infra-red transmission of highly iodine-doped polyacetylene films

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The physical properties of polyacetylene films are strongly modified by doping and in particular its optical absorption drastically increases in the middle infra-red range. The aim of this report is to study the behaviour of infra-red transmission between 4000 and 400 cm^{-1} when doping $(CH)_x$ with iodine. It is shown that the excess absorption due to the dopant is a reversible phenomena, however the *cis* to *trans* isomerization induced by doping remains. Elsewhere we have studied the evolution of the transmission at a very high doping level, up to twenty per cent of dopant, and showed that even in the metallic range ($\simeq$six per cent of dopant) some short *cis* sequences exist. Consequently this is evidence that doping is a less efficient isomerization process than thermal treatment.

Keywords Polyacetylene; doping; infra-red transmission; isomerization

INTRODUCTION

A considerable amount of work has been done on the physical properties of undoped and doped polyacetylene films in recent years[1]. Such interest was enhanced by the potential applications of semiconducting or conducting $(CH)_x$ as an electronic material. An essential characteristic of this polymer is the existence of two isomeric forms: *cis* and *trans* (*Figure 1a* and *b*); the *cis* being unstable and the *trans* stable. A number of papers[2-4] have described a *cis–trans* isomerization induced by thermal treatment or doping. However, although the thermal treatment leads to a 'pure' product easily available for electrical and optical studies, it was shown that the thermal *cis* to *trans* isomerization induces the creation of a number of defects which lead to partial destruction of the product if the treatment is performed at too high a temperature ($T > 140$°C), over too long a time period, or if the treatment is performed at too low a temperature $T \simeq 100$°C giving incomplete isomerization, the *cis* to *trans* ratio depending on T.

However, it was proved that the characteristic *cis* bands disappear after doping. However as the absorption coefficient strongly increases, especially between 600 and 1000 cm^{-1} nothing can be deduced from usual samples ($\simeq 200$ to 10 μm thick) as soon as the doping level reaches 1%.

In order to establish the effects of doping on the *cis–trans* isomerization, essentially by a study of the middle infra-red bands attributed[5] to the *cis* and *trans* isomers, we have carried out two types of experiment: first a transmittance study of thin (~ 5 to 1 μm) initially *cis* $(CH)_x$ films during iodine doping and then during the dopant desorption. Then, using high sensitivity apparatus described later, we have studied the evolution of the *cis* and *trans* bands when doping thin (~ 5 to 1 μm) films up to 20%.

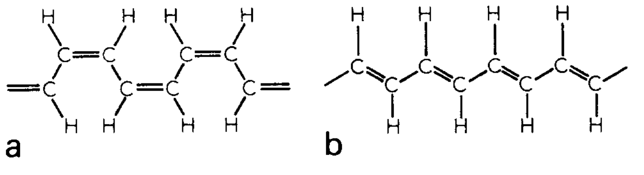

Figure 1 Schematic structure of the two $(CH)_x$ isomers (a) *cis*, (b) *trans*

Our goal is to determine, in connection with previously published results obtained by various techniques, the isomerization processes and related behaviour of the polyacetylene structure (fibril and chain behaviour) during the doping-induced isomerization.

EXPERIMENTAL TECHNIQUES

Sample preparation and doping

Polyacetylene films were obtained by the method described by Ito *et al.*[6] The experimental polymerization conditions were as follows: the solvent was pentane, molar ratio Al/Ti = 4 with a Ti concentration of 0.4 mol l^{-1}, temperature -78°C and acetylene pressure 0.1 atmospheres.

The thin films were directly grown onto the vertical surfaces of the reactor wetted by the catalyst solution. After cleaning the film was detached from the glass by immersion in pentane giving thin sheets, the thickness of which ranged between 1 and 5 μm; they were then kept at -20°C.

The iodine doping was performed in the liquid phase using pentane solutions of iodine at various concentrations. The dopant content was measured by film weight uptake and is always given in the molar ratio I/CH as a percentage.

The dopant desorption was obtained by making a sandwich of the doped $(CH)_x$ film between two copper sheets, the system being plunged in pentane to avoid air oxidation.

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Apparatus

Two types of apparatus were used:

(1) Perkin Elmer 577 spectrophotometer used for middle infra-red transmission in the range 4000 to 400 cm^{-1} down to a 10^{-2} transmission level.

(2) An infra-red compact grating spectrometer specially built in order to measure transmissions as low as 10^{-6}. This apparatus is extensively described elsewhere[7] and so we only report here its essential characteristics.

In the middle infra-red range, the 300 K background emission is often the greatest limitation of photoconductive detectors. To reduce this effect a grating spectrometer was built, cooled with liquid nitrogen incorporating a Ge:Cu detector, the temperature of which is kept near 4.2 K. The main characteristic of this spectrometer is the noise equivalent power corresponding to the total radiation noise which was found to be 10^{-12} W $\mathrm{Hz}^{-1/2}$; that is about two orders of magnitude lower than the golay detector. This apparatus works in the range 2500 to 400 cm^{-1} and allows an ultimate transmittance measurement of 5.10^{-7} near 1500 cm^{-1}. It was essentially used to determine the transmittance of highly doped $(\mathrm{CH})_x$ films.

RESULTS

Low iodine doped samples

In *Figure 2* the infra-red spectra of a *cis* rich undoped $(\mathrm{CH})_x$ film are shown; whose thickness is ~1 μm as can be deduced from the interference fringes observed on curve A. When the dopant amount increases we successively note (curves B, C, D, E, F): the disappearance of the fringes; the increase in absorptivity and the appearance of the two strong characteristic bands of the dopant: a broad band around 800 cm^{-1} and a narrow band at 1380 cm^{-1}. As soon as the dopant content reaches 4% (curve G) the transmittance becomes negligible. However, the rapid disappearance of some of the *cis* bands (1800 cm^{-1}, 1330 cm^{-1} and 440 cm^{-1}) is noticeable.

Dopant desorption spectra

These spectra are reported in *Figure 3* where the lower curve corresponds to a 5% doped sample. On increasing the desorption treatment we note the disappearance, or at least strong intensity decrease of the dopant bands at 1370 cm^{-1} and ~300 cm^{-1} as well as the reappearance of the

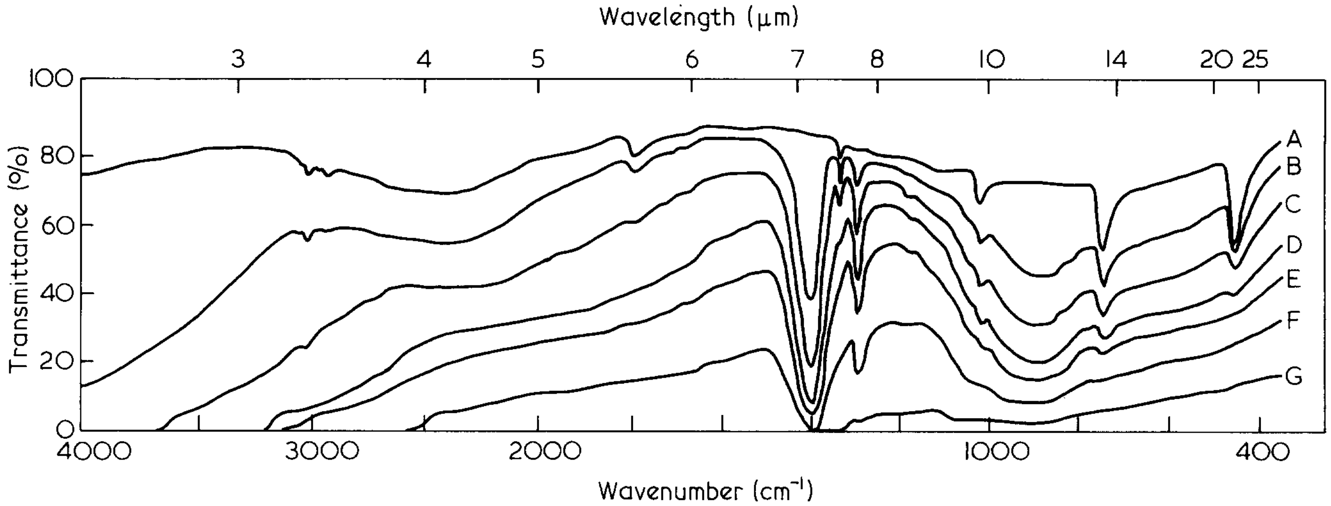

Figure 2 Infra-red spectra of a *cis* rich $(\mathrm{CH})_x$ film at various iodine doping stages

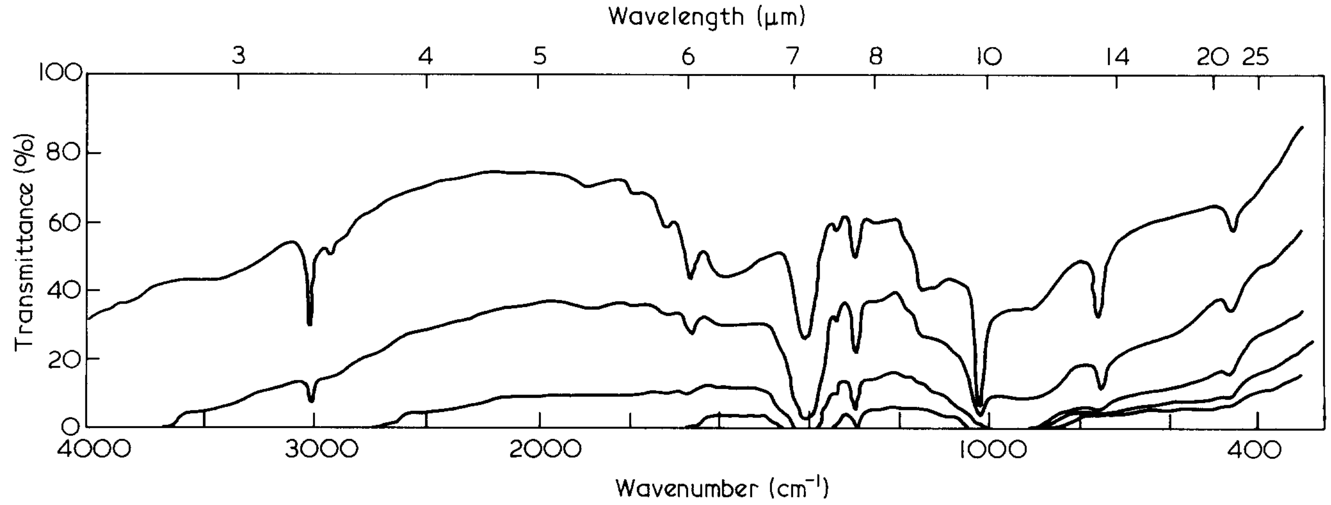

Figure 3 Infra-red spectra of an iodine-doped sample after various dopant desorption times

trans bands, especially at 3010 cm^{-1} and ~1000 cm^{-1}.

Elsewhere some of the *cis* bands have disappeared entirely (3030 and 1800 cm^{-1}) however the 740 cm^{-1} *cis* band remains and to a lesser extent the 440 cm^{-1} band. Finally after ten days desorption (upper curve) the amount of dopant is so small that it cannot be measured by any weight increase (<0.1%).

Highly doped samples transmission

Two sample thickness were studied, 1 μm and 5 μm. For the 5 μm samples *Figures 4* and *5* respectively exhibit the *cis* and the *trans* doped transmittances in the range 2500 to 400 cm^{-1} for various doping levels up to 8%. (At higher dopant concentrations we cannot point out the transmittance over the whole range).

In *Figure 4* we can clearly see, on the upper curve (1.7%) the well known characteristic bands of the dopant (1380 cm^{-1} and ~800 cm^{-1}) and the presence of two *cis* bands (740 and 440 cm^{-1}) are also distinct. When increasing the dopant concentration we observe a strong decrease in the *cis* band at 440 cm^{-1}, however the 740 cm^{-1} *cis* band does not decrease significantly. At a doping level of 8% we note the disappearance of the *cis* band (440 cm^{-1}) and the fact that the bottom of the dopant band cannot be reached at 1380 cm^{-1} (transmittance lower than 10^{-7}).

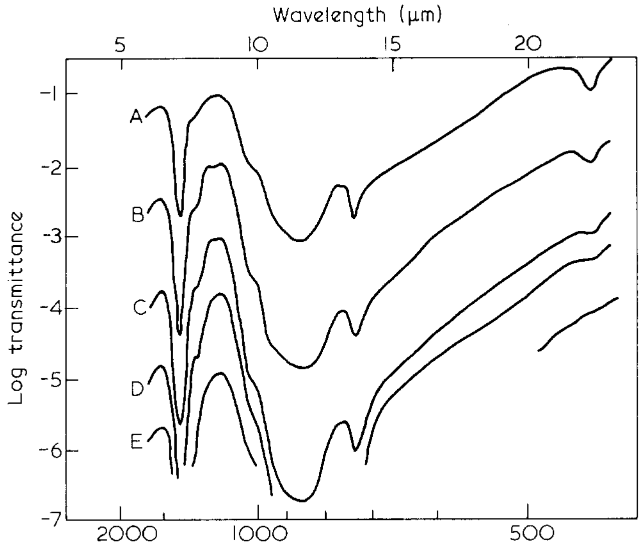

Figure 4 Infra-red spectra of a 5 μm thick *cis* $(CH)_x$ film iodine-doped up to 8%. (A), 1.7%; (B), 3.5%; (C), 5.3%; (D), 6%

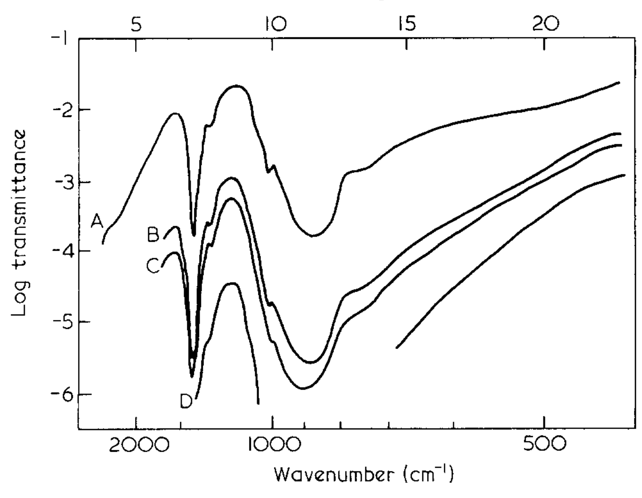

Figure 5 Infra-red spectra of a 5 μm thick *trans* $(CH)_x$ film iodine-doped up to 8%. (A) 2.3%; (B) 4.5%; (C) 6%; (D) 8%

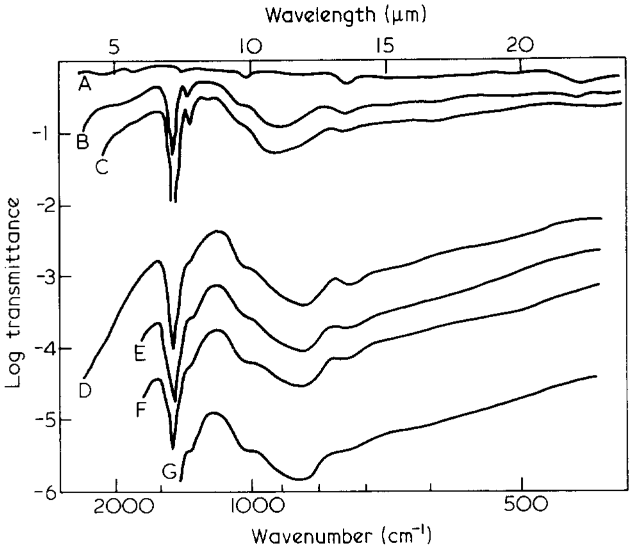

Figure 6 Infra-red spectra of a 1 μm thick *cis* $(CH)_x$ film iodine-doped up to 20%. With perkin elmer 577: (A) 0%; (B) 1.5%; (C) 2.2%. With cold spectrometer: (D) 7%; (E) 9%; (F) 13%; (G) 20%

When using thermally isomerized (10 min at 140°C) polyacetylene films (*Figure 5*) the overall behaviour is quite similar however it is noticeable that with the first curve (2.3% dopant) the residual *cis* bands have disappeared.

Figure 6 shows the curves obtained from *cis* $(CH)_x$ film of thickness $\simeq 1.5$ μm with similarities to that of the 5 μm sample but with this thinner film we could measure the transmittance up to 20% dopant concentration (such a doping level corresponds to the saturation of the film, i.e. $\simeq 15\%$ including any existing amount of interfibrillar dopant not removed). We note the disappearance of the 440 cm^{-1} band when the dopant concentration reaches 2% and that of the 740 cm^{-1} between 13% and 20%.

DISCUSSION

Firstly we shall review the main results pointed out by this experimental work:

(a) From the transmittance measurements with the Perkin Elmer apparatus: (1) During the doping process we observed an overall increase in the absorption and noted the dopant bands (1380 cm^{-1} and 800 cm^{-1}) as well as the *cis–trans* isomerization exhibited by the increase in the number of *trans* bands and decrease in the number of *cis* bands. (2) During the dopant desorption; we noted that the doping effect was partially reversible. The overall absorbance decreases as well as the typical dopant bands; but the overriding phenomena was that the number of *trans* bands appeared to increase and the number of *cis* bands were much lowered and some even disappeared (440 cm^{-1}).

(b) From the results obtained with the cold grating apparatus: (1) With film thickness around 5 μm, 8% dopant is necessary to destroy the 440 cm^{-1} *cis* band with the other *cis* band remaining. However, thermal treatment at 140°C for a few minutes gives a better isomerization. (2) With 1 μm thick films, with a 2% dopant level the 440 cm^{-1} *cis* band disappears, and with a 13% dopant level the 740 cm^{-1} *cis* band also disappears.

We shall now try to analyse the results summarized above: From section (a) concerning doping and dopant desorption it follows that doping is a reversible phenomena concerning its own bands and its effects on *trans* $(CH)_x$. However, the isomerization that doping induces is irreversible (with respect to the word 'reversible' we assume that the dopant can be removed and that after one cycle of high doping the $(CH)_x$ film will retain almost all its properties. However, we think that various doping and desorption cycles modify the properties of the film with respect to its microscopic morphology and mechanical behaviour).

Concerning section (b) relating to highly doped samples, the results are quite similar. We noted the disappearance of the 440 cm^{-1} band; an effect which can be easily explained by the attribution of the 440 cm^{-1} band to a longitudinal –C–C–C– stretch whereas the 740 cm^{-1} is a C–H deformation. Consequently if the dopant (low level) produces the isomerization of some parts of a long *cis* chain this can lead to short enough *cis* sequences to affect the 440 cm^{-1} band but not the 740 cm^{-1} (C–H vibration) which can subsist only if some short *cis* sequences remains (at a high doping level).

With regard to the discrepancy observed between the curves in *Figures 4* and *5* where the previous bands disappear at a lower dopant level in the 1 μm thick film than on the 5 μm film, we can explain this by the phenomena of inter- and intra-fibril dopant diffusion[8].

Across the thick (5 μm) film, some dopant concentration inhomogeneity can exist leading to a less doped medium zone in which the *cis* isomer subsists. In addition the intrafibrillar diffusion is not as high in the thick film both from the previous assumption but also taking into account that the fibril diameter is much lower in the thin (1 μm) film due to a shorter polymerization time. That such a fibril diameter increases with the polymerization time has already been pointed out[9,10]. Consequently the intrafibrillar dopant diffusion needs a longer time when increasing the fibril diameter and even when the mean value of the dopant concentration reaches 5% the central part of strong fibrils remains in the *cis* form.

CONCLUSION

We have shown that the excess absorption due to the dopant, in $(CH)_x$ films, is a reversible process as well as the bands characteristic of the dopant; however, the *cis* to *trans* isomerization obtained by doping remains. Elsewhere the evolution of infra-red transmittance was pointed out even at a high doping level showing that some *cis* sequences subsist even in the metallic range of polyacetylene.

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