

# Physical properties of polyacetylene films doped with $\text{MoCl}_5$ and $\text{WCl}_6$

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(Received 17 June 1981)

The physical properties of polyacetylene  $(\text{CH})_x$  are considerably modified by doping with halogens ( $p$  type) or alkalis ( $n$  type). In this paper we present the effects of new kinds of dopants — salts of transition metals such as  $\text{WCl}_6$  and  $\text{MoCl}_5$ . Dopant diffusion inside the film, the electrical behaviour and the infra-red transmission are studied and compared with effects produced by usual dopants. They have low diffusion coefficients and readily produce large dopant concentration using salt solutions.

**Keywords** Polymer; polyacetylene; spectroscopy; conductivity; doping; profiles

## INTRODUCTION

Polyacetylene  $(\text{CH})_x$ , the simplest conjugated polymeric system available as flexible films, is an extensively studied material. Its physical properties are considerably modified by a doping process, particularly its electrical and optical behaviour. A number of  $n$  and  $p$  type dopants have now been discovered<sup>1,2</sup> and their influence on the polymer pointed out<sup>3</sup>. In this paper we study the effect of new dopants of polyacetylene; derivatives of transition metals. In a recent paper<sup>4</sup> we showed that  $\text{MoCl}_5$  and  $\text{WCl}_6$  are catalytic systems for the polymerization of  $\text{C}_2\text{H}_2$ . We also pointed out that the polymers so prepared showed greater conductivity than those obtained with the usual catalysts  $\text{Ti}(\text{OBU})_4$ – $\text{I}(\text{Et})_3$ .

From this we realize the  $(\text{CH})_x$  doping with  $\text{MoCl}_5$  and  $\text{WCl}_6$  and then study the dopant diffusion in the polymer, the behaviour of the electrical conductivity and infra-red transmission *versus* the dopant concentration. The results are compared with those already known. The main point lies in the fact that their diffusion coefficients in  $(\text{CH})_x$  are lower than those of previous dopants, their stability is higher and a large range of dopant concentrations may be easily obtained and controlled.

## EXPERIMENTAL

Polyacetylene films were prepared by the Shirakawa's technique using the catalytic system  $\text{Al}(\text{Et})_3$ – $\text{Ti}(\text{OBU})_4$  in toluene at  $-78^\circ\text{C}$  in order to obtain the *cis* isomer. Sample thicknesses were: 150  $\mu\text{m}$  for the Castaing microprobe analysis and electrical conductivity measurements, 50  $\mu\text{m}$  for the visible study. In the latter case the film thickness is measured by mean of scanning electron microscopy. The samples were doped using a solution of  $\text{MoCl}_5$  or  $\text{WCl}_6$  in toluene; various concentrations being used, ranging from a saturated solution ( $S$ ) down to a  $10^{-2} S$  solution. When thick films (150  $\mu\text{m}$ ) are used the dopant content is measured by weight uptake, but for the infra-red measurements the

doping is too light to be measured by weight uptake and the dopant content is related to the doping time in a solution. Finally we used very thin films ( $\approx 0.1 \mu\text{m}$ ) directly polymerized onto a glass substrate for the visible transmission, where even a high doping level cannot be measured.

Dopant profiles through the samples were measured by means of Castaing microprobe analysis (CAMECA MS 46 type apparatus), the detailed experimental procedure being described in an earlier publication<sup>5</sup>. Electrical conductivity was studied from 77K up to 300K for a large range of dopant concentration ( $10^{-3} < y < 10^{-1}$ ) in the formula  $[\text{CH}(\text{WCl}_6)_y]_x$  or  $[\text{CH}(\text{MoCl}_5)_y]_x$ ; measurements were performed by the usual four probe technique, gold wires being fastened with electrodag paste. Middle infra-red transmission measurements were performed with a Perkin Elmer 577 spectrophotometer and a visible study on a Beckman Acta M IV apparatus.

## RESULTS

### Dopant profiles

Figure 1 shows typical dopant profile (W in  $\text{WCl}_6$ ) through a 150  $\mu\text{m}$  thick sample. Firstly we notice a strong dopant gradient between the surface (high concentration) and the middle (low and even null concentration) which proves the non-uniformity of the dopant concentration. Secondly a non-symmetry appears in this profile; this effect can easily be related to the difference in the  $(\text{CH})_x$  films morphology surfaces. On Figure 2 we have reported various dopant profiles of W obtained after various doping times in a saturated solution of  $\text{WCl}_6$  (the films are characterized both by the doping time and the mean value  $y$  of dopant content). We observe that a very long doping time is necessary to obtain an almost uniform dopant concentration ( $t = 6 \times 10^5$  s). This leads to a relatively small dopant diffusion coefficient which can approximately be estimated to  $10^{-10} \text{ cm}^2 \text{ s}^{-1}$  (compared to the iodine diffusion  $D \approx 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ).

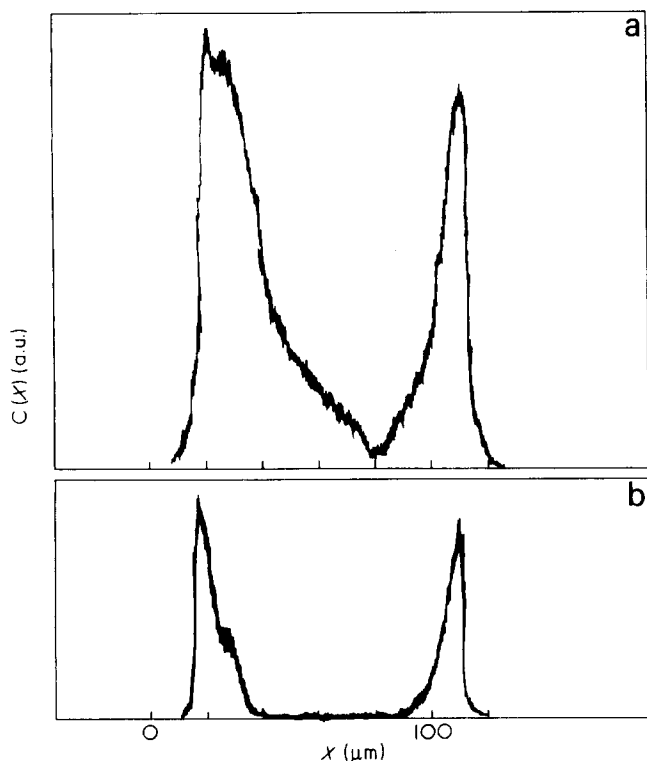


Figure 1 W profiles through  $\text{WCl}_6$  doped  $(\text{CH})_x$  films: (a)  $[\text{CH}(\text{WCl}_6)_{0.003}]_x$ ; (b)  $[\text{CH}(\text{WCl}_6)_{0.013}]_x$

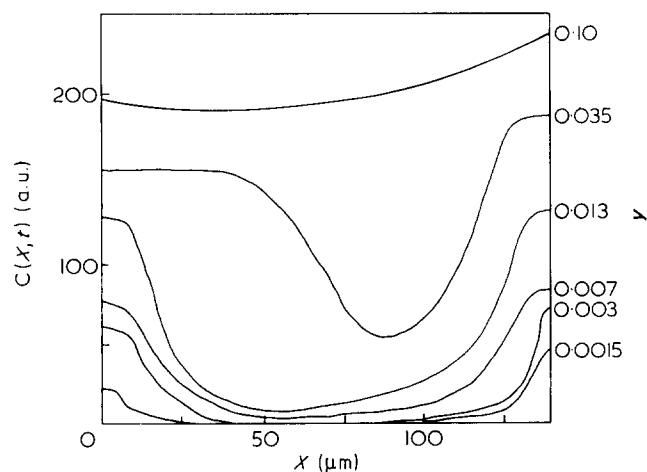


Figure 2 W profiles through  $\text{WCl}_6$  doped polyacetylene for a large doping time ( $t$ ) range: ( $t = 10''$ ,  $y = 0.0015$ ,  $t = 30''$ ,  $y = 0.003$ ,  $t = 100''$ ,  $y = 0.007$ ,  $t = 300''$ ,  $y = 0.013$ ,  $t = 20000''$ ,  $y = 0.035$ ,  $t = 600000''$ ,  $y = 0.10$ )

Electrical conductivity

The maximum conductivity, obtained for  $y=0.1$  in both cases, lies around  $\sigma \approx 200 \Omega^{-1} \text{cm}^{-1}$ . Figure 3 shows that the dopant concentration dependence of the conductivity is quite similar to those obtained with usual dopants. Figures 4 and 5 respectively, exhibit the electrical resistivity variations of  $\text{MoCl}_5$  and  $\text{WCl}_6$  doped  $(\text{CH})_x$  films, versus  $10^3/T$ .

A semiconducting behaviour is observed—the dependence is not linear particularly at low temperatures—however we can deduce (at high temperatures) an activation energy which decreases strongly when dopant concentration increases reaching about 8.8 meV for  $[\text{CH}(\text{MoCl}_5)_{0.1}]_x$  (the results are reported in Figure 6).

Middle infra-red and visible transmission

Figure 7 shows a series of transmission through a  $50 \mu\text{m}$  thick film for various doping times, i.e. at various (increasing) dopant concentrations of  $\text{MoCl}_5$ . A strong, but narrow, absorption appears at  $1380 \text{ cm}^{-1}$  where the transmission becomes rapidly negligible, and a broad absorption band lies between  $850$  and  $950 \text{ cm}^{-1}$ . The other bands appearing at  $1720$  and  $1680 \text{ cm}^{-1}$  are attributed to the film oxidation. Similar results were

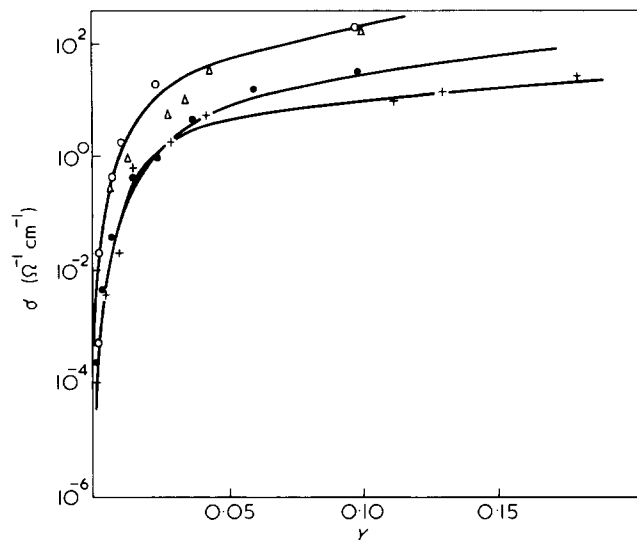


Figure 3 Electrical conductivity versus dopant concentrations. (+)  $\text{CF}_3\text{SO}_3\text{H}$ ; (●)  $\text{SbF}_5$ ; ( $\Delta$ )  $\text{WCl}_6$ ; (○)  $\text{MoCl}_5$

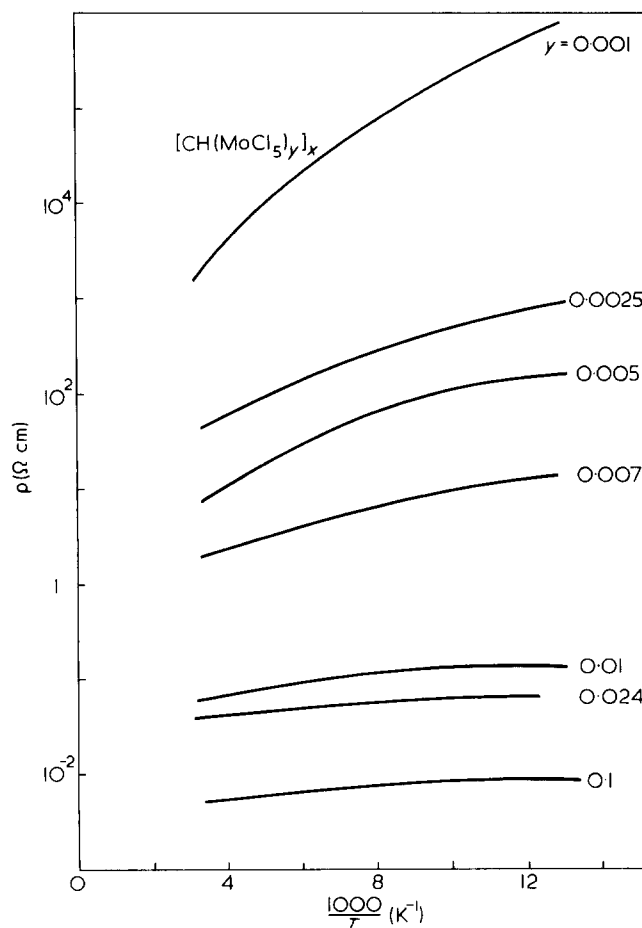


Figure 4 Electrical resistivity of  $[\text{CH}(\text{MoCl}_5)_y]_x$  samples versus  $10^3/T$  for various dopant concentrations  $y$ .

obtained with  $\text{WCl}_5$  doped samples in which case (vacuum performed experiments) we verified that the  $1720\text{ cm}^{-1}$  and  $1680\text{ cm}^{-1}$  bands do not appear.

However, the  $450\text{ cm}^{-1}$  band (*cis* isomer band) decreases slightly when the dopant concentration increases; this indicates a light *cis-trans* isomerization induced by doping. It appears that a much higher dopant concentration is necessary to produce further isomerization of the polymer. Note that the *cis-trans* isomerization also appears on the  $3010\text{ cm}^{-1}$  (*trans*) and  $3050\text{ cm}^{-1}$  (*cis*). The additional absorption over the undoped sample is reported in Figure 8 where we observe excess absorption coefficients around  $0.11\text{ eV}$  and at  $0.173\text{ eV}$  (the excess absorption near  $0.195\text{ eV}$  may be attributed to the film oxidation). Finally we used infra-red

measurements in order to study the polyacetylene evolution during the dopant desorption process. Data are reported in Figure 9 where: curve (1) corresponds to the undoped *cis* rich  $(\text{CH})_x$  film ( $65\text{ }\mu\text{m}$  thick), curve (2) to the lightly  $\text{MoCl}_5$  doped film and curves (3), (4) to the same film respectively wetted in toluene during 20 minutes and 850 minutes in order to obtain a dopant desorption. We mainly observe: an increase of the transmission over the whole range studied and especially near  $1380\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ , that is to say in the absorption bands due to the dopant. However the effect of the dopant on the absorption bands of the *cis* and *trans* isomers are not reversible and we chiefly observe this effect on the ( $450, 750$  and  $3050\text{ cm}^{-1}$ ) *cis* bands whose intensities are reduced by the doping; while the  $1000\text{ cm}^{-1}$  *trans* band is enhanced.

Near infra-red and visible transmissions were measured on very thin films ( $\approx 1000\text{ \AA}$  thick) directly polymerized onto a glass substrate. The film was doped in a saturated  $\text{MoCl}_5$  solution in toluene for various times. From these measurements the evolutions of the absorption coefficient versus photon energy for various dopant concentrations are plotted in Figure 10. We notice a double maximum around  $1.9$  and  $2.1\text{ eV}$  which persists even at high dopant levels; however, another maximum of the absorption coefficient increases during the doping process in all the range ( $1-3\text{ eV}$ ) between  $10^5$  and  $3 \times 10^5\text{ cm}^{-1}$ . Finally we

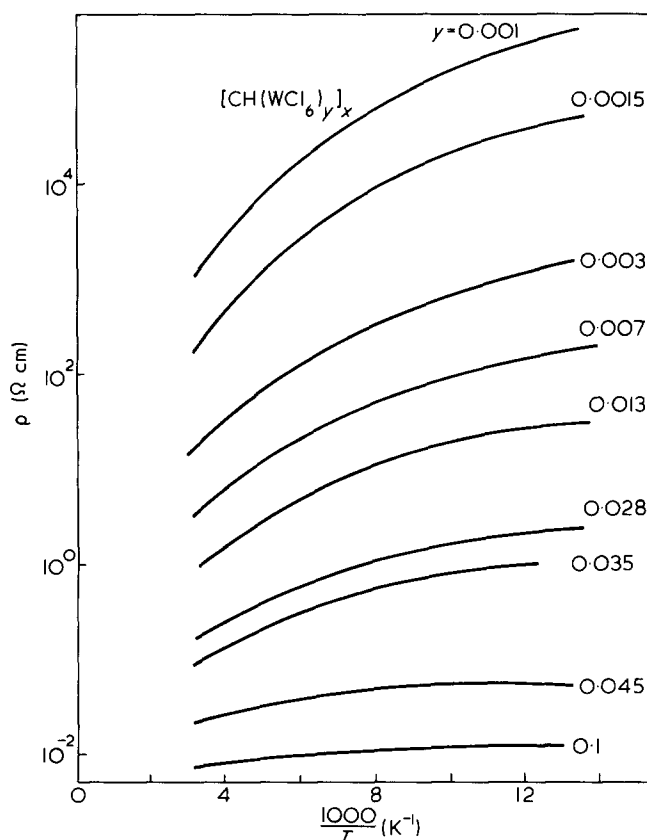


Figure 5 Electrical resistivity of  $[\text{CH}(\text{WCl}_6)_\gamma]_x$  samples versus  $10^3/T$  for various  $\gamma$  values

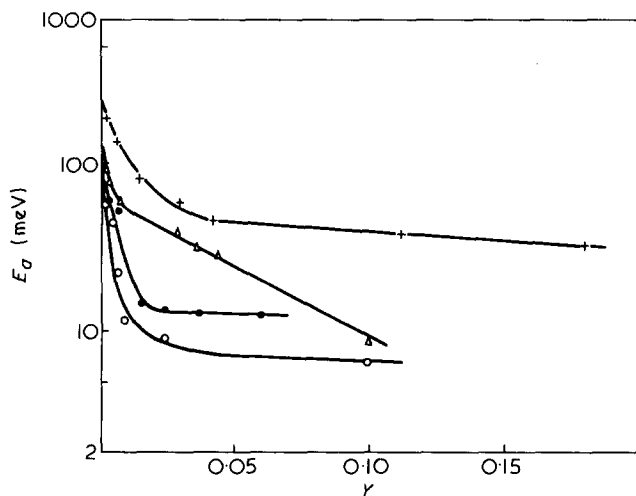


Figure 6 Dopant concentration dependence of electrical activation energy in  $(\text{CH})_x$  film. (+)  $\text{CF}_3\text{SO}_3\text{H}$ ; (●)  $\text{SbF}_3$ ; (Δ)  $\text{WCl}_6$ ; (○)  $\text{MoCl}_5$

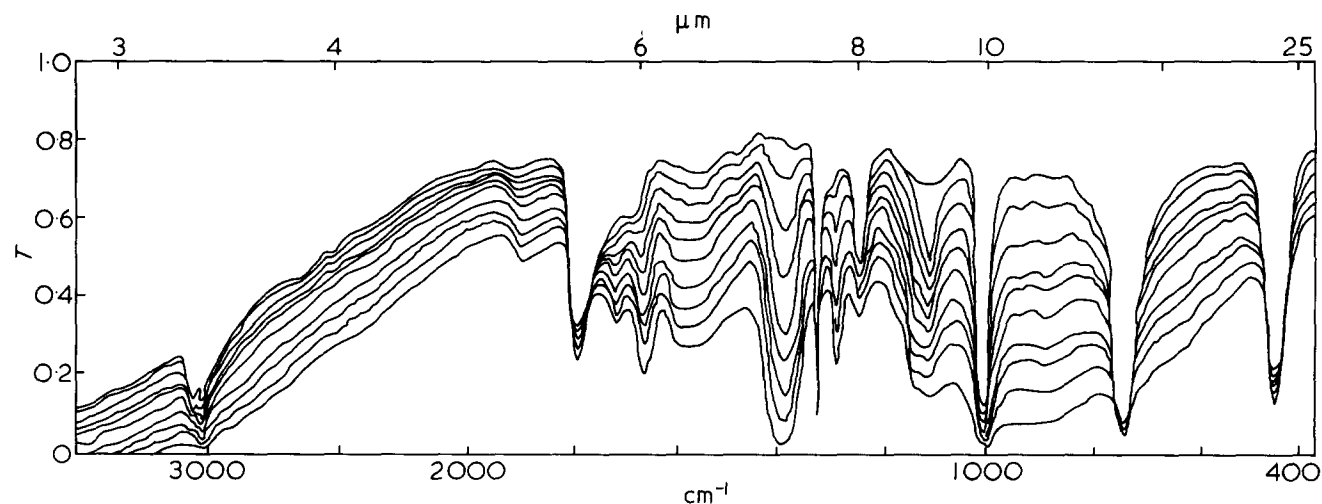


Figure 7 Middle infra-red transmission of light  $\text{MoCl}_5$  doped  $(\text{CH})_x$  film at various dopant stages

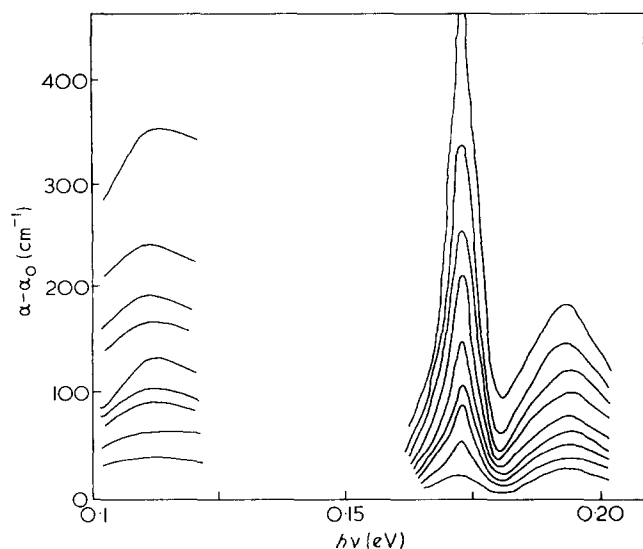


Figure 8 Additional absorption (over undoped samples) deduced from Figure 7 results

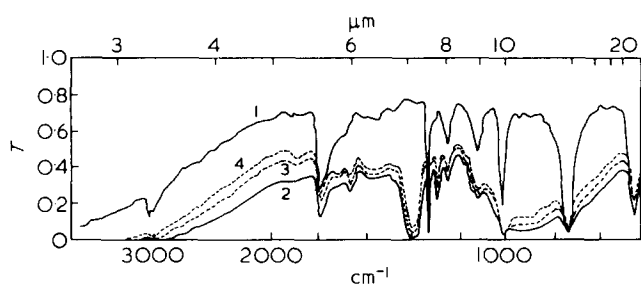


Figure 9 Middle infra-red transmission at various dopant ( $\text{MoCl}_5$ ) desorption stages

must notice that, in such a thin film some inhomogeneities can exist in the film thickness ( $\approx 0.1 \mu\text{m}$ ). Therefore we assume a general evolution of the absorption coefficient more than its absolute value.

### DISCUSSION

First the microprobe analysis of the dopant profiles shows that there is a dopant inhomogeneity through the sample thickness due to the dopant diffusion; but as the surface concentration greatly increases with the doping time, and also from the discrepancy between the observed profiles and the usual erf functions, obtained from Fick's Laws we can deduce that the diffusion is not the only effect observed but that a physical adsorption of dopant molecules also takes place on the polymer fibrils; this result was pointed out elsewhere<sup>6</sup>. An advantage of  $\text{WCl}_6$  is its low diffusion coefficient ( $D \approx 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ )<sup>8</sup> (results obtained with  $\text{MoCl}_5$  and other transition metals seem to be similar). From those first results we can expect that those salts may be more stable dopants than those already known.

The effect of  $\text{WCl}_6$  and  $\text{MoCl}_5$  on the electrical conductivity of  $(\text{CH})_x$  films is quite similar to those obtained with iodine or  $\text{SbF}_5$ <sup>9</sup>: a large increase in conductivity (12 orders of magnitude) is observed, especially between  $y=0$  and  $y=0.01$ , and the deduced activation energy exhibits a semiconductor to metal transition around  $y \approx 10^{-2}$ . The departure from the straight line in the curves  $\text{Log } \rho = f\left(\frac{10^3}{T}\right)$  at low

temperatures is larger than those observed with  $\text{SbF}_5$  dopant, and with  $\text{I}_2$  or  $\text{CF}_3\text{SO}_3\text{H}$  this effect is relatively negligible: if we compare the diffusion coefficient of such dopants we observe that  $D_{\text{CF}_3\text{SO}_3\text{H}} \approx D_{\text{I}_2} > D_{\text{SbF}_5} > D_{\text{WCl}_6}$ . Therefore the gradient of dopant concentration through the sample increases when  $D$  decreases and at low temperatures the thin high doped surface sides produce a more conductive part than the thick low doped central part of the sample. Such an effect could explain the non-linear behaviour observed at low temperatures and dopant concentrations. Concerning the optical properties the effects already observed<sup>10</sup> with the 'usual dopants' appear here, for the middle infra-red transmission as well as for the visible transmission and particularly the narrow band at  $1380 \text{ cm}^{-1}$  and the broad band around  $850 \text{ cm}^{-1}$ . We note the *cis-trans* isomerization induced by doping; however this effect seems to be small on these lightly doped samples and it might be interesting to study the evolution of the *cis* to *trans* ratio versus the dopant concentration.

The desorption experiments showed the reversibility of the middle infra-red transmission in all the range except for the parts concerning the polyacetylene bands, giving a confirmation of the non-reversibility of the *cis-trans* isomerization.

### CONCLUSION

We reported the first results concerning polyacetylene films doped with transition metal salts as  $\text{WCl}_6$  and  $\text{MoCl}_5$ , and showed that all the studied properties such as the electrical conductivity, infra-red and visible absorptions presented similar behaviour to the usual dopants of this polymer; however it seems that this study, which must be extended to the other transition metal salts, has given some interesting results.

These dopants make it possible to obtain easily a very large range of dopant concentrations, especially for low doping levels, by using dilute solutions. Their low diffusion coefficients allow us to obtain more stable systems. Finally it seems that all 'dopants' of  $(\text{CH})_x$  lead to

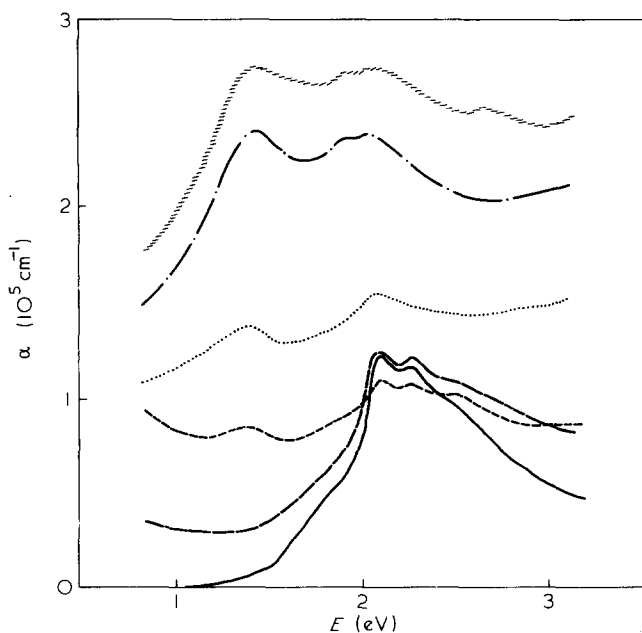


Figure 10 Near infra-red and visible absorption coefficient of undoped and  $\text{MoCl}_5$  doped  $(\text{CH})_x$  film

quite identical effects on its physical properties and we think that the knowledge of the largest possible number of polyacetylene dopants may be of some interest in order to understand the physical part played by these species on the polymer.

#### ACKNOWLEDGEMENT

Financial support from DRET under contract No. 78/1259 is gratefully acknowledged.

#### REFERENCES

- 1 Chiang, C. K., Park, Y. W., Heeger, A. J., Shirakawa, H., Louis, E. J. and MacDiarmid, A. G. *J. Chem. Phys.* 1978, **69**, 5098
- 2 'The physics and chemistry of low dimensional solids', (Ed. L. Alcacer), Proceedings of the NATO ASI, Tomar (Portugal), Sept. 1979, D. Reidel Pub.
- 3 Chiang, C. K., Gau, S. C., Fincher, C. R., Park, Y. W., MacDiarmid, A. G. and Heeger, A. J. *Appl. Phys. Lett.* 1978, **33**(1), 18
- 4 Aldissi, M., Linaya, C., Sledz, J., Schue, F., Giral, L., Fabre, J. M. and Rolland, M. *Polymer* (in press)
- 5 Aldissi, M. *Thèse d'Etat* 1981, Montpellier University (France)
- 6 Benoit, C., Rolland, M., Aldissi, M., Rossi, A., Cadene, M. and Bernier, P. Submitted to *Phys. Stat. Sol.*
- 7 Berniere, F., Haridoss, Louboutin, Aldissi, M. and Fabre, J. M. *J. Phys. Chem. Sol.* (in press)
- 8 Rolland, M., Aldissi, M., Bresse, J. F., Benoit, C. and Cadene, M. Submitted to *Phys. Stat. Sol.*
- 9 Rolland, M., Bernier, P., Aldissi, M., Linaya, C., Selds, J., Schue, F., Fabre, J. M. and Giral, L. *J. Phys. Lett* 1980, **41**, 165
- 10 Fincher, C. R., Ozaki, M., Heeger, A. J. and MacDiarmid, A. G. *Phys. Rev.* 1979, **19**(8), 4140